# 研究業績集
## (1970~2010)

２０１１年３月

長崎大学
環境科学部
環境材料化学研究室

富永義則

# 主要研究業績の概要

１９７０年に長崎大学に入学して以来、アメリカ合衆国、カナダ、それに台湾と長期の海外出張を含め、４５年間長崎で過ごすことになった。長崎大学に入学すると、いきなり学生運動の嵐に巻き込まれ、この事件は大学卒業まで影響を及ぼし正常の卒業式もないまま卒業した。この間教養部の授業には興味が持てず、また毎日毎日のクラス討論会にも何か違和感を感じつつ時を過ごしていたような感じがしている。このとき有機化学（井本稔:有機電子論）のセミナーが始まった。全く正規の講義とは違い、それぞれのセミナー参加者が調べたことを発表していく、大学で学ぶという事はこのような勉強だと思った。このような有機化学のセミナーが数年続いた。講義で習う内容よりも遥かに豊富であったと今でも思っている。これまで遊び惚けていた大学生活を一変させ２年の後半から実験に没頭した。この事がきっかけとなり、大学とは、学問とは、社会とは、といった事を真剣に考えたような気がする。人より遅いスタートになったが真剣に勉強した。実験も面白かった。２年生や３年生でも大学院生の先輩から教わるでもなく、またその大学院生でも自分流で実験していたように思っている。参考書や文献を頼りに与えられた課題に向けて自分なりに進めていった。このころから我流になっていた。卒業研究に入る頃には恩師の小林五郎先生の人柄、研究方針等等理解できるようになり、この先生のためなら少しでも役にたてると思っていた。機会あるごとに聞いた『良い仕事をしようぜ』の一言。この一言で今日まで来た。大学院に進む頃には小林先生のライフワークはケテンジチオアセタールの合成研究になっていたと思う。そのケテンジチオアセタールの研究を私自身定年になるまで続けられた事に故小林五郎先生に心より感謝したい。私の力量不足で、本来なら世界的な研究になる課題でありながら、十分に発展させる事ができなかったことに申し訳なく思っています。

長崎大学薬学部薬化学研究室での卒業研究から大学院修士課程、それに日本学術振興会奨励研究生と小林五郎先生に指導を受け、今日までに得た成果の概要を示しておく。

【エナミノジチオカルボン酸誘導体の研究】

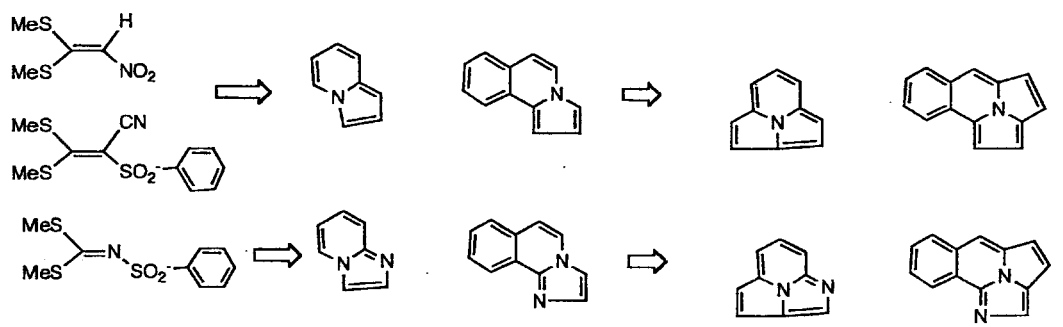
ケテンジチオアセタール合成の際使用する二硫化炭素はフリーデルクラフト反応などの溶媒としてのみの使用でなく合成試薬、特に含硫複素環化合物の環状構築剤としても重要である。薬化学研究室では小林五郎教授が長崎大学に赴任されて以来ピリジン *N*-オキシドやインドール誘導体の研究が活発に展開されていた。二硫化炭素も各種インドール誘導体も豊富に研究室にあった。これらの試薬を使用して展開し博士

ートさせてもらった事に感謝するとともに、幸運だったと思う。

このケテンジチオアセタールはもちろん小林五郎先生のライフワークでもあり、また私のライフワークでもある。

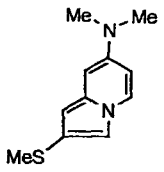
多種多様なタイプがデザインされ有機合成化学分野で多用されているケテンジチオアセタールは、活性メチレン化合物に塩基存在下二硫化炭素を作用させ、適当なアルキル化剤でアルキ化して得られる求電子試薬である。世界中で研究されているケテンジチオアセタールの中で、インドの Junjappa やアメリカの Dieter のグループのケトン基、ドイツのグループのシアノ基やスルホニル基を持つケテンジチオアセタールの研究が有名である。各種生理活性天然物や合成医薬品の中に、また最近では各種デバイス等の機能性材料に広く応用されている複素環化合物の合成にこれらケテンジチオアセタールを利用する以下のような研究を行ってきた。

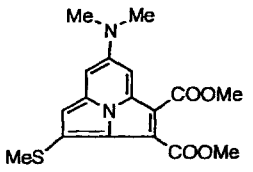
1） カルボリンやピロロインドール等の縮合インドール誘導体の研究
2） 2-ピロンおよび2-ピリドン誘導体の研究
3） ピリミジンおよびピラゾロピリミジン誘導体の研究
4） インドリジンやサイクラチン誘導体の研究
5） その他、チラン、フラン、ピロール、チオフェン、ピリジン、キノリン等の複素環化合物

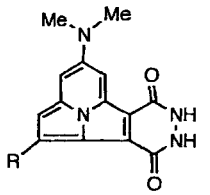


【チオフェン誘導体の研究】

アメリカ合衆国の Castle 教授や Lee 教授との共同研究による多環性チオフェン誘導体の研究。多くのチオフェン誘導体が種々の化石燃料に含まれ地質学的に、また環境に対する影響、特に人体に対する影響等を知るためには個々のチオフェン誘導体の構造を知る必要がある。これらチオフェン誘導体の個々の性質を詳しく知るためには、それぞれのチオフェン誘導体を合成して、ある程度の量を確保する事が必要になってくる。Castle 教授のもとで可能な限り天然化石燃料に含まれている 150 種ほどの全チオフェン誘導体の合成が検討された。そのうち 2 年間で７０種ほどを合成した。

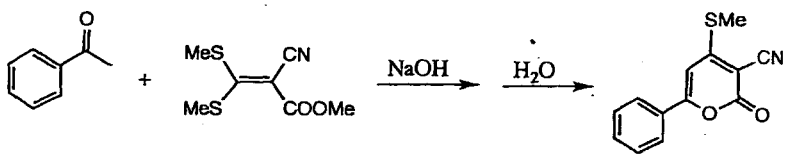


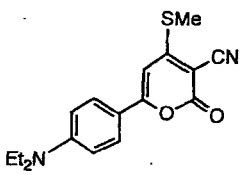



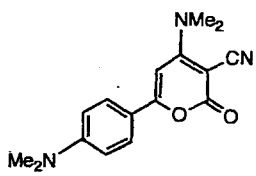

【蛍光性 2-ピロンおよび2−ピリドン誘導体の合成研究】

ケテンジチオアセタールと活性メチレン化合物との反応で得られる各種 2-ピロン誘導体が固体状態で強く発光し有機 EL 材料としての可能性がでてきた。このピロン誘導体の中には固体状態ばかりでなく溶液状態でも強く発光する化学物がある。このように著者らが見いだした蛍光性ピロン誘導体は溶液でも固体でも強く発光し今後の応用が期待される。現在は2−ピリドン誘導体への展開も計っている。

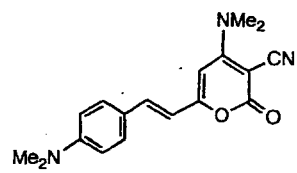



λ-472nm
Em-543 nm
ϕ=0.95




λ-412nm
Em-487 nm
ϕ=0.17




λ-513nm
Em-610 nm
ϕ=0.01

# 近代化学史

長崎大学環境科学部：富永義則

明治の初め近代日本が確立されて行くとき、それまでにない急激な改革で一部混乱もみられるが、これほど見事に欧米の諸制度を消化し定着させた先人達の功績は大きい。結果的には良かったかもしれない徳川幕府によるおよそ３００年間の鎖国政策後、急激な欧米化にともない文物や諸制度が流入し、また導入されて行ったのもそれなりの受け皿があってのことである。医学や薬学それに化学も同じで、出島を中心にした日蘭交流２５０年の間にこの受け皿となるべく土台が築かれていった。それらの大きな役割を担ったのがオランダ商館員やその商館医達で、またその仲介役の通詞達であった。その結果、幕末長崎に海軍伝習所が設置され、また養生所が併設された。その中で化学も実学として確立されて行くのである。医学の知識が導入されると同時に、それを理解するための化学も同時に輸入された。最初に導入された化学は、病気の仕組み、医薬品の成分、それらを理解するためのものであった。

人、風景をそのまま写し取る写真機がフランスで最初に応用されたのが１８３９年です。それが日本に伝わり（１８４８年)、実際日本人の手で写真が取られるのが１８５８年、そして職業写真として開業されたのが１８６２年である。

世界、特にヨーロッパを中心に発達してきた化学の知識、技術がそれ程時間を経ないで、鎖国下の日本に伝えられてきた事がその後の日本の近代化に役に立っている。日本人の勉強好きもさることながら、出島で展開されたオランダの人々の真摯な交友による事は間違いない事実である。

## 第１章　明治前化学の科学史的意義と時代区分

西洋の近代自然科学の意味での化学は、ギリシャ以来の知的伝統と、ルネサンス以降の社会的発展とを背景として成立したものである。科学の社会的関係の観点から観察すれば、自然研究の一要素としての科学研究にはまず社会的要求が存在し、一方職業的な知的行動としての自然研究の伝承がある。そしてこれらの活動を保証する意図をもった科学アカデミーのような制度が成立したのは十七世紀のことである。その時期以降の西欧における化学史は、主として化学現象の基本法則の発見の歴史を根幹としている。この歴史は産業技術の発展と互いに関連し、化学法則の発見は新しい化学技術をよびおこし、化学技術はまた逆に化学法則の発見を促してきた。

このように大きく発展してきた西洋と同じ類型の化学史を、明治前日本に求める

ことは不可能である。明治前日本の化学について、まずかたることのできるのは、西欧自然科学の一部分としての化学が、本邦に移植され、これがやがて知識の伝統をつくるに至った過程である。この過程の中で、近代科学の意味ににおける西洋で確立していた「研究」や「実験」の体系の跡を見い出す事は、おそらく不可能であろう。ただ我々は移植された知識体系が社会の実際的需要に支えられて、日本文化の中に小規模ながら質的には重要な一つの位置を占めるに至った事実を観察することができる。その事実なしに明治期における、職業的化学者の出現、また化学の「研究」の歴史の開始はあり得なかった。この意味において明治前化学史は単なる、「移植」の記載ではなく、近代日本文化形成の前史の一部分として重要な意味をもつ。

**近代化学の始まり**

近代自然科学としての化学：ギリシャ以来の知的伝統とルネサンス以降の社会的発展）
自然研究の一つの要素としての化学研究
　社会的要求
　職業的な知的行動としての自然研究の伝承
　　科学アカデミーのような制度……１７世紀
　　化学現象の基本法則の発見<———>産業技術の発展
　西洋自然科学の一部分としての化学の日本への移植———知識の伝統
　知識体系———社会の実際的需要に支えられてーーー日本文化の位置
　近代日本文化形成の前史の一部分として重要

**第一期（西洋化学の啓蒙期）**

宇田川玄真撰、宇田川榕庵校補『遠西医方名物考』（１８２２年：文政５年）
青地林宗：『気海観瀾』（１８２７年：文政１０年）
宇田川榕庵：『植学啓減原』（１８３５年：天保６年）
宇田川榕庵：『舎密開宗』（第一巻出版；１８３７年：天保８年）
　１８世紀にラブオアジエが確立した化学の知識体系を完全に導入
　化学用語法の確立
　化学物質の識別・保存・製造・精製等———実際的知識の提供

島　立甫：『舎密開宗・外篇』（１８４６年：弘化３年）
川本幸民：『気海観瀾広義』（１８５１年：嘉永４年）

**第二期（実用的化学的活動期）**

諸藩や幕府による諸施設の創設（化学的活動の職業化、製造所と試験所を兼ねる）
福岡藩精煉所（１８４７年：弘化４年）
島津藩精煉所（１８５０年：嘉永３年）
佐賀藩反射炉築造（１８５０年：嘉永３年）
幕府：蕃書調所の開設（１８５７年：安政４年）１８６０年精煉方設置
　　開成所（１８６３年）　　１８６５年化学方
　　長崎に分析究理所（１８６４年：元治元年）
　　ポンペ；ボードイン；ハラタマ等化学の講義と実技伝習、それに精錬所における技術指導

著作活動
川本幸民：『化学新書』（１８６０年：万延６年）原子論を基礎とする。
河野禎造：『舎密便覧』化学分析指針（１８６５年安政３年）
上野彦馬：『舎密局必携』（１８６２年：文久２年）
　　化学の理論と実験の部を簡潔に要約：最初の実験化学書

**西洋化学の導入**
『和蘭局法』宇田川玄真訳
『和蘭薬鏡』宇田川榛斉訳、宇田川榕庵篇
『和蘭薬性辨』藤林泰助訳
『依白乙薬性論』青地林宗訳：（１８２３年：文政６年）
『新訂増補和蘭薬鏡』宇田川玄真訳、宇田川榕庵校補（１８２８年：文政１１年）
『製煉発蒙』坪井信道訳（１８２９年：文政１２年）

**『気海観瀾』の化学的内容**
（青地林宗：１８２７年：文政１０年）概括的な物理学常識書
　化学の基礎知識についても若干紹介
　物質構造に関して１７、１８世紀自然科学の量子論を紹介
気体の物理的性質を述べた後「気種」について説明
　「気種」として「窒気」＝窒素ガス；「精気」＝酸素ガス；「燃気」＝水素ガス；
　「硬気」＝炭酸ガス
「燃気」鉄屑や亜鉛から生ずる
水素ガスと酸素ガスとの反応を述べ、生成物は水であると述べている。
化学物質：硝石、————

「鉛質」や「鉄質」の検出に硫化カルシュムでの検出法がある。
「験水」として「塩質」の有無を石鹸の泡立ち、硝酸銀溶液での濁色で検査

**『植学啓原』の化学の位置づけ**

植物学の体系と方法を簡潔かつ本格的に要約
宇田川榕庵：（１８３５年：天保６年）
動物と植物は物質変化に関する学の助けによってはじめて研究される。
自然界の諸物を外形に従って区別、分類する学を優先。
生物研究の方法として化学を重視
例
炭化水素：暗にいわゆる炭水ガスは炭素に水素を与え親和してガスをなすものなり。二種あり。その一つは炭素。名を第一炭水ガスという。炭素７—５３—８—５。水素２—４６—１—５。その２、炭素多く、名づけて第２炭水ガスという。また生油ガスという。炭素８—４—８—６—５。水素１—５１—３５。共にベリュウスの質測による。

**『遠西医方名物考』：化学の基本概念の導入**

宇田川玄真撰、宇田川榕庵校補（１８２２年：文政５年）
榕庵の「舎密開宗」に先立って化学を体系的に述べた最初の文献
「酸化物」
諸物は酸素と抱合すれば酸性となり酸味を生ず。然るに多くの酸素を帯びて酸味なきものありこれを酸化物という。あるいは水は酸素と水素を抱合して生じ。酸味の諸物に比すれば酸素多しといえども少しも酸味なきがごとし。ゆえに水は水素の酸化物とす。然るに酸物と酸化の区別は酸素の多少に因らずただその抱合せる物体の異なるに因る。あるいは酸化物も多く酸素を帯びれば酸性となるものあり。たとえば酸化リンに多く酸素を多く含めばリン酸となるがごとし。諸物燃焼すればこれに大気の酸素を引いて酸化す。すなわち金属酸化のごとし。

**『舎密開宗』**

宇田川榕庵：１０才代から蘭学を学び生涯化学の研究に携わる。１９歳で訳書。
１８２８年—１８４３年：日本」各地の温泉を調査、化学成分の定性分析——
『温泉試説』『西洋鉱泉譜』
２２歳：和蘭薬鏡初篇三巻
２５歳：遠西医方名物考

３１歳：新訂増補和蘭薬鏡
３６歳：植学啓原
４０歳：舎密開宗

内編１８巻、外編３巻（内編２１巻、外編１５巻の予定）

**『舎密開宗』の原著**

Elements of Experimental Chemistry(1796 年に初版)：ヘンリー（William Henry 1774-1836）マンチェスターの化学者、気体の溶解度の研究で有名
直接の原本：イペイ(A.Ypey)によるオランダ語重訳本{Ypey, Adolphus:Sijistematisch Handboek der Scheikunde (Amsterdam, 1804-1811)}
参考文献２０余冊
『舎密原本：ラボイシール、1800』:ラヴォアジェの世界的名著（Traite Elementaire de Chimie: Paries, 1789）の蘭訳
本書の理論はラヴォアジェの化学体系。ドルトン原子仮説は取り扱われていない。

化学発達の歴史＝化学史の記述がある
初巻―第１５巻：無機化学
第１６、１７、１８巻：機性体（有機物質）
外編：化学分析
著者自身の実験に裏付けられている

目次
巻１
１：舎密親和、２：溶解、３：温気進溶解、４：溶解促解散、５：溶解難易、６：撹拌進溶解、７：親和須水、８：甲乙頼丙親和、９：飽充、１０：親和変物性、１１：単親和、１２：複親和、１３：温素、１４：温素廓物容、１５：温素増減、１６：温素好平均、１７：温素導達、１８：煮沸熱度、１９：凝流気三体、――――
巻４
７２：炭酸亜爾加里、７３：炭酸和加里、７４：炭酸加里性質、７５：剥篤亜斯（ポットアス）、７６：測剥篤亜斯之炭酸法――――
巻５
９２：硫酸加里、９３：硫酸加里稟性、７４：硫酸曹達、――――――

語彙比較（かっこ内は『舎密開宗』）

法則（法則）、性質（稟性）、分解（分離）、試薬（試薬）、乾法（燥道の法）、無機物（無機性体）、有機物（機性体）、燃焼（熱焼）、成分（成分）、容積（容積、体容）、重量（秤量）、比重（異類重）、ガス（瓦斯）、蒸気（蒸気）、固体（凝体）、液体（流体）圧力（圧力）、温度（温度）、沸騰（沸騰）、沸点（沸点）、————
煮沸（煮沸）、蒸留（蒸留）、振盪（振盪）、撹拌（撹拌）、結晶（結晶）、潮解（潮解）、溶液（溶液）、濾過（濾過）、飽和（飽和）、昇華（昇華）、装置（装置）、他

元素５５個について記述
「光素」＝光、「温素」＝熱、「越列機素」＝電気
酸素、水素、窒素、炭素
代表的な金属は現在の名前と一致

**理論的概念**

１．化学親和力
２．燃焼
３．酸・塩基・中和
４．酸化と還元
５．雷金（雷酸金）の組成
６．亜量（当量）

**『気海観瀾広義』川本幸民**（１８５１年、嘉永４年）
青地林宗の**『気海観瀾』**に仮名交じりの注解を附したもの
初等物理学の教科書
元素・単体・化合物
「せーみに於いては引力を親和力と名づく。親和力とは物体の表面相引き接するを謂うふにあらず。諸物質相合して更に一体を成すを謂ふなり。凡万物諸異成分成分元素より成る者多し。これを合体又複体と云う。又一同成分より成って異類の物を混ぜざる者あり。これを単体と云う。諸金。炭素。気類の元素。光素。温素等。これなり。古人は唯水火気土を元素として、４元行と称す。然れども近来此四物皆合体なる事を知りしより。其の説全く廃す」
酸素、酸、塩基、塩、中和等の解説

**『兵家須読舎密真玄源』**
川本幸民訳、１８５６年（安政３年

化学の基礎の初歩的解説。砲工学用教科書
元素の化学的性質がデーヴィ＝ベッルセリウスの電気化学的二原論で説明
倍数比例の法則が電気化学的二原論の形式に従って述べられている。
「抱合重量」は「アトームゲヴィグテン」原子量と定義されている。
酸素を百とする原子量

| | |
|---|---|
| 酸素 | 100.00(16.03:16.00) |
| 水素 | 6.24(1.00:1.00) |
| 窒素 | 88.61(14.20) |
| 硫黄 | 201.17(32.23) |
| 燐素 | 196.14(31.43) |
| 蘇魯留母 | 221.33(35.47) |
| 炭素 | 76.44(12.25) |

**『万宝新書』**

宇田川興斉訳。１８６０年（万延元年）
幕末期における化学の翻訳、学習が、産業・軍事の必要を背景として進められたことはこれまで述べた通り。
日常生活や職人の手技にかかわるヨーロッパの新しい技術に関する知識の大衆化が進められて、これが化学的実際知識の普及に寄与。
化学書ではなく、手工業、農業、医療、生活の諸般にわたる技術を「初篇」１３８項目、「二篇」１３４項目
「藍青を硫酸にて溶解する法」「錫をもって白顔料を製する法」「青色墨汁を製する法」――

**『舎密便覧』**

河野貞造訳、１４冊（安政３年）
定性分析化学の専門書で金属根（越歴多爾増極体）と酸根（越歴多爾減極体）の分別検出法。元素（単体）化合物（抱合体）の試薬に対する固有反応を図表で示し、呈色反応には手彩色を施し、分析用機具を図示している。
金属根には灼熱試験、木炭吹管分析を用い、「本試法」は現行の定性分析の方式と同じく硫化水素等の分離法を挙げている。

**『舎密局必携』**

上野彦馬抄訳、１８６２年（文久２年）初篇３冊

原子論にもとづく初歩の理論的知識と化学物質の性質製法を平易に述べている。

巻一　舎密総括

第１章　舎密原素及び親和平衡力

第２章　実形体及び気形体の異重力

第３章　異顕温

第４章　塩基

第５章　酸類

第６章　舎密親和

第７章　越列機消極体及び積極体

第８章　舎密所業

第９章　舎密区別

第１０章舎密力徳

第１１章尺度量術

同無機性舎密篇　非金属部

第１２章酸素

第１３章水素

第１４章炭素

第１５章硫黄

巻二　無機性舎密篇　非金属篇

第１６章摂列紐母（セレニウム）

第１７章窒素

第１８章格羅耳（コロール）

第１９章蒲羅密烏母（ブロミュム）

第２０章沃陳（ヨジウム）

第２１章弗律阿留母（フリュオリュム）

第２２章燐

第２３章砒

第２４章勃留母

巻三　無機性舎密篇　非金属部

第２５章　シリシュム

付録

摂影術（ポトガラヒー）

摂影石版術

６４種の元素名をイロハ順に列挙
「水素１個の率と定め比較」親和平衡力（化学当量）を表示
反応式を用いている

幕末の化学の状態
**宇都宮三郎と化学**
セメント工業の創設、工業技術指導者
尾張藩士上田帯刀に西洋砲術を学ぶ「海上砲術全書」

**長崎の化学**
**海軍伝習所（１８５５～１８６０年）**
ファン・デン・ブルックによる化学教授
大通詞品川藤兵衛、小通詞西慶太郎、本木昌造、楢林栄左衛門、小通詞並塩谷種三郎、町医師吉雄圭斉などが、Dr van den Broek から分離（化学）、窮理（物理）、測量、算術、石炭坑等々、それぞれに応じて学修する事を命じられる。

**医学伝習における化学教授**
海軍伝習に医学伝習が加えられる。
１８６０年「養生所」――＞精得館（１８６１年）
**ポンペ・ファン・メールデルフォールト**（Pompe van Meerdervort）
(東印度会社官医兼自然科学調査官) ブルクの後任として医学のカリキュラムに基礎学として化学・物理学を講義
司馬凌海：『七新薬』
太田雄寧『新式化学』

**分析究理所**
ポンペの後任ボードウイン（A.F.Bauduin 文久２年）医学教育から物理、化学を基礎教育として分離
「分析究理所」設立を進言（１８６４）
ハラタマ（W.K.Garatama）1866 年長崎に着任

# The Synthesis and Properties of Polycyclic Aromatic Thiophenes and Related Heterocycles Occuring in Coal-derivtived Products

**Raymond N. Castle* [1], Marvin L. Tedjamulia, Yoshinori Tominaga [2]
Ram Pratap [3], Michiharu Sugiura[4] and Hirotaka Kudo**

Department of Chemistry, University of South Florida,
Tampa, FL 33620 USA

**Milton L. Lee, Masatomo Iwao [5] and Robert D. Thompson [6]**

Department of Chemistry, Brigham Young University,
Provo, UT 84602 USA

**Gary E. Martin [a], Robert T. Gampe, Jr.[a], M. J. Musmar [a]
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**Stanford L. Smith and W. John Layton**

Department of Chemistry, University of Kentucky,
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**Ralph E. Hurd and LeRoy F. Johnson**

Nicolet Magnetics Corporation, 255 Fourier Avenue
Fremount, CA 94539 USA

**Lectures in Heterocyclic Chemistry, VII, 1-50 (1984)**

**1984**

# Synthesis of Heterocyclic Compounds Using Nitro Ketene Dithioacetals

**Yoshinori Tominaga and Yoshiro Matsuda**

**Faculty of Pharmaceutical Sciences, Nagasaki University,**
**1-14, Bunkyo-machi**
**Nagasaki 852,**
**Japan**

***J. Heterocyclic Chem.*, 22, 937-949 (1985)**

**1985**

# Synthesis of Cycl[3.2.2]azine and Benzo[*g*]cycl[3.2.2]azine Derivatives by Use of the [2 + 8]Cycloaddition Reaction of Indolizines and Dimethyl Acetylenedicarboxylate

**Yoshinori Tominaga, Yoshihide Shiroshita, Tomihiko Kurokawa, Hiromi Gotou, Yoshiro Matsuda, and Akira Hosomi**

**Faculty of Pharmaceutical Sciences, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan**

*J. Heterocyclic Chem.*, 26, 477-487 (1989)

**1989**

# Synthesis of Heterocyclic Compounds Using Carbon Disulfide and Their Products

**Yoshinori Tominaga**

**Faculty of Pharmaceutical Sciences, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan**

(Dedicated to Professor Ernest Campaigne on the occasion of his 75th birthday)

*J. Heterocyclic Chem.*, **26, 1167-1204 (1989)**

**1989**

# Polarized Ethylenes. IV
# Synthesis of Polaraized Ethylenes Using Thioamides and Methyl Dithiocarboxylates and Their Application to Synthesis of Pyrazoles, Pyrimidines, Pyrazolo[3,4-*d*]pyrimidines, and 5-Aza[2.2.3]cyclazines

**Yoshinori Tominaga, Yoshiki Matsuoka, Yukio Oniyama, Yoshimitsu Uchimura, Hirofumi Komiya, Michiyo Hirayama, Sinya Kohra, and Akira Hosomi**

**Faculty of Pharmaceutical Sciences, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan**

*J. Heterocyclic Chem.*, 27, 647-660

**1990**

# S-Silylmethyl-substituted Ketene Dithioacetals as Synthetic Equivalent of a Novel 1,3-Dipolar Reagent, Alkyldenethiocarbonyl Ylide; Synthesis and [3+2]Cycloaddition Reactions

Yoshinori Tominaga,[a] Satoshi Takada,[a] and Shinya Kohra[b]

[a]Faculty of Pharmaceutical Sciences, [b]Faculty of Liberal Arts, Nagasaki University
1-14, Bunkyo-machi, Nagasaki 852, Japan

*Tetrahedron Letters*, 35(21), 3555-3558 (1994)

1994

# *N*-Bis(methylthio)methylene Derivatives. VII. Syntheses and Reaction of Synthetic Equivalents of New 1,3-Dipolar Regents Using *N*-Bis(methylthio)methylene Derivatives

**Yoshinori TOMINAGA, Koichiro OGATA, Hiroshi UEDA, Shinya KOHRA, and Akira HOSOMI**

**Faculty of Pharmaceutical Sciences,[a] Faculty of Liberal Arts,[b] Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan, Department of Chemistry, University of Tsukuba,[c] Tsukuba, Ibaraki 305, Japan.**

*Chem. Pharm. Bull.*, 43(9), 1425-1434 (1995)

1995

# Synthesis and Chemiluminescence of 1,3-disubstituted Pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazine-5,8(6*H*, 7*H*)-diones and Related Compounds

**Yoshinori Tominaga,[a]* Noriko Yoshioka,[a] Seigo Kataoka,[a] Norihito Aoyama,[b] Toshiyuki Masunari,[b] and Akira Miike,[b]**

[a]Faculty of Pharmaceutical Sciences, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan,
[b]Kyowa Medex Co. Ltd, 1-8-5 Shinkawachuo-ku, Tokyo, Japan

*Tetrahedron Letters.*, 36(47), 8641-8644 (1995)

1995

# Synthesis of Methylthiomaleimides for the Preparation of Pyridazines and Related Compounds.

**Yoshinori Tominaga**

Center forInstrumental Analysis, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852-8521, Japan

**Yasuhiro Shigemitsu**

Industrial Technology Center of Nagasaki, 2-1303-8 Ikeda,
Omura, Nagasaki 856-0026, Japan

**Kenji Sasaki**

Faculty of Pharmaceutical Sciences, Okayama University,
Tsushima, 1-1-1, Okayama 700, Japan

*J. Heterocyclic Chem.*, 39, 571-591 (2002)

**2002**

# Cyclazines
# (Product Class 7)

Yoshinori Tominaga

**Sciences of Synthesis**
**(Method of Molecular Transformation)**
**Vol. 7, p1025-1078**

**Georg Thieme Verlag KG**

**2003**

# Synthesis of Dimethyl Heterocyclic-o-Dicarboxylates Using Dimethyl Acetylenedicarboxylate

**Yoshinori Tominaga and Kazuo Ueda**

**Faculty of Environmental Studies, Nagasaki University,
Bunkyo-machi, 1-1-14, Nagasaki 852-8521,
Japan**

*J. Heterocyclic Chem.*, **42, 337 (2005)**

**2005**

# Synthesis and Steady-State Spectroscopic Study of 5-Aryl-2,2'-bipyridyls. New Fluorescent Compounds in Solid State

Naoko Mizuyama,[1] Yoshinori Tominaga,[1*] Shinya Kohra,[1] Kazuo Ueda,[1] Shun-ichi Hirayama,[2] and Yasuhiro Shigemitsu[3]

[1]Faculty of Environmental Studies, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521,
[2]Sasebo National College of Technology, 1-1 Okishin-machi, Sasebo 857-1193,
[3]Industrial Technology Center of Nagasaki, 2-1303-8 Ikeda, Omura 856-0026

*Bull. Chem. Soc. Japan*, 79(4), 602-611 (2006)

2006

# One-pot Synthesis of Polysubstituted Pyridine Derivatives Using Ketene Dithioacetals

Masayori Hagimori, Naoko Mizuyama, Yukari Hisadome,
Junko Nagaoka, Kazuo Ueda,
and Yoshinori Tominaga

Faculty of Pharmaceutical Sciences, Nagasaki International University, 2825-7,
Huis Ten Bosche, Sasebo 859-3298, Japan.
Faculty of Environmental Studies, 1-14, Bunkyo-machi,
Nagasaki 852-8521, Japan.
Faculty of Engineering of Nagasaki University, 1-14, Bunkyo-machi,
Nagasaki 852-8521, Japan

***Tetrahedron*, 63, 2511-2518**

**2007**

# List of Papers

Yoshinori Tominaga

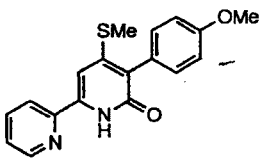
Nagasaki University

Faculty of Environmental Studies

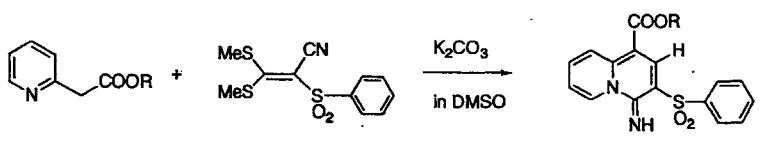
(1970~2010)

平成22年12月16日

1) **A Novel Small Molecule Fluorescent Sensor for $Zn^{2+}$ Based on Pyridine-Pyridone Scaffold.** Hagimori, Masayori; Mizuyama, Naoko; Yasuchika, Yamaguchi; Hideo, Saji; Tominaga, Yoshinori. Faculty of Pharmaceutical Sciences, Nagasaki International University, 2825-7, Huis Ten Bosch, Sasebo, Japan. *Talanta*, (2010), Accepted date: 2-12-2010. **Abstract**----The development of a water-soluble and small molecular weight fluorescent probe, 3-(4-methoxyphenyl)-4-(methylsulfanyl)-6-(pyridin-2-yl)pyridin-2(1*H*)-one (3), for detecting $Zn^{2+}$ based on pyridine-pyridone skeleton is reported. We observed a clear chelation enhanced fluorescence effect of 3 in the presence of $Zn^{2+}$. Other fluorescent properties of 3 are discussed.




2) **Novel Synthesis of 4*H*-Quinolizine Derivatives Using Sulfonyl Ketene Dithioacetals.** Hagimori, Masayori; Matsui, Sayaka; Mizuyama, Naoko; Yokota, Kenichirou; Nagaoka, Junko; Tominaga, Yoshinori. Faculty of Pharmaceutical Sciences, Nagasaki International University, 2825-7, Huis Ten Bosch, Sasebo, Japan. *European Journal of Organic Chemistry* (2009), (33), 5847-5853. Publisher: Wiley-VCH Verlag GmbH & Co. KGaA, CODEN: EJOCFK ISSN: 1434-193X. Journal written in English. AN 2009:1390515 CAPLUS **Abstract**----In the synthesis of 4H-quinolizine derivs. involving the use of a sulfonyl ketene dithioacetal, we found a novel reaction in which the remaining methylsulfanyl group was replaced with a proton after the ring-closure reaction in the quinolizine skeleton under mild conditions, without the use of any metallic reagent. The reaction of 3,3-bis(methylsulfanyl)-2-phenylsulfonyl-acrylonitriles (1a,b) with 2-pyridylacetonitrile (2a) in the presence of potassium carbonate as a base in DMSO afforded 4-imino-2-methylsulfanyl-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitriles (3a,b). The methylsulfanyl group at the 2-position of 3a,b was readily removed under methanol reflux conditions to afford 4-imino-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitriles (4a,b) in good yields. Alkyl 3-phenylsulfonyl-4*H*-quinolizine-1-carboxylates (4c-f) were directly synthesized from sulfonyl ketene dithioacetal (1a,b) with alkyl 2-pyridylacetates (2b,c) and involved desulfanylation by simple hydrolysis. In addn., the fluorescent properties of these compds. were investigated. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009).
KD-136: Fluorescence-24: Citing 0.

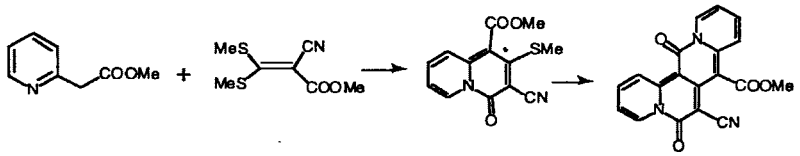



3) **Synthesis and TDDFT investigation of new maleimide derivatives bearing pyrrole and indole ring.** Shigemitsu, Yasuhiro; Komiya, Kaori; Mizuyama, Naoko; Hagimori, Masayori; Tominaga, Yoshinori. Industrial Technology Center of Nagasaki, 2-1303-8, Ikeda, Omura, Nagasaki, Japan. *Research Letters in Organic Chemistry* (2009), No pp. given. Publisher: Hindawi Publishing Corp., CODEN: RLOCB3 ISSN: 1687-6938. http://www.hindawi.com/journals/rloc/2009/413219.pdf Journal; Online Computer File written in English. AN 2009:1181147 CAPLUS **Abstract**---A novel series of heterocycles were obtained through the condensation reaction of 4-methylthiomaleimides with pyrroles and indoles. The newly synthesized compds. exhibit their major electronic absorption peaks ranging 435-504nm in soln. at room temp. Time-dependent d.-functional theory (TDDFT) calcns. were systematically performed in order to elucidate their structure-color relationships, using a set of exchange-correlation (XC) functionals. The TDDFT computational scheme employing PCM-TDDFT/6-31+G(d,p)//DFT/6-311G(d,p) level of theory gave qual. satisfactory results in their λmax predictions.
KD-135: Citing 0.

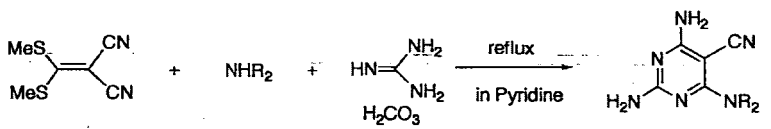
4) **Development of optoelectronics materials based on molecular design of photofunctional compounds.** Shigemitsu, Yasuhiro; Tominaga, Yoshinori; Araki, Koji. Dep. Ind. Mater., Industrial Technology Center

of Nagasaki, Omura, Japan. *Nagasaki-ken Kogyo Gijutsu Senta Kenkyu Hokoku* (2009), Volume Date 2008, **38**. 52-54. Publisher: Nagasaki-ken Kogyo Gijutsu Senta, CODEN: NGSHEU ISSN: 0916-6726. Journal written in Japanese. AN 2009:1141572 CAPLUS **Abstract**----Mol. crystal of 2,2':6',2"-terpyridine has a very interesting property to have much different emission characteristics between the two crystal structures. While type N plate crystal shows very strong fluorescence, type P needle crystal and amorphous mol. do not. Application for reversible light-switching devices is expected. This report describes quantum chem. calcns. to clarify the theor. basis of the reversible switching.
KD-134:Fluorescence-23: Citing 0.

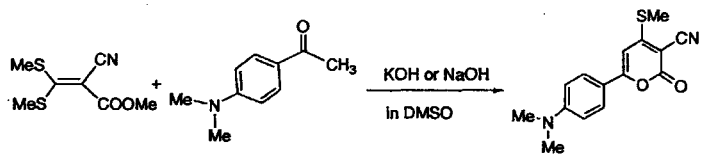
5) **Synthesis of quinolizino[3,2-*a*]quinolizine derivatives and their fluorescence.** *Heterocycles*, (2009), 78(5), 1271-1279. Yokota, kenichirou, Hagimori, Masayori; Shigemitsu, Yasuhiro; Mizuyama, Naoko; Wang, Bo-Cheng; Tominaga, Yoshinori. Faculty of Pharmaceutical Sciences of Nagasaki International University, 2825-7, Huis Ten Bosch, Sasebo, Japan. *Heterocycles* (2009), 78(3), 555-570. Publisher: Japan Institute of Heterocyclic Chemistry, CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. **Abstract**---- Polycyclic quinolizine derivatives, quinolizino[3, 2-*a*]quinolizines (4a-c), were synthesized in moderate yields by a one-pot method using ketene dithioacetal, methyl bis(methylsulfanyl)-methylenecyanoacetate (2), alkyl 2-pyridylacetates (1a, b), and 2-pyridylacetonitrile (1c). Compounds 4a, b exhibited red fluorescence (Em max: 576 nm) in solid state.
KD-133: Fluorescence-22: Citing 1.




6) **One-pot synthesis of 6-substituted amino-2,4-diaminopyrimidine derivatives using ketene dithioacetals with amines and guanidine carbonate.** Miki Hirose, Masayori Hagimori, Yasuhiro Shigemitsu, Naoko Mizuyama, Bo-Cheng Wang, and Yoshinori Tominaga. Faculty of Pharmaceutical Sciences of Nagasaki International University, 2825-7, Huis Ten Bosch, Sasebo, Japan. *Heterocycles* (2009), 78(4), 899-903. Faculty of Pharmaceutical Sciences of Nagasaki International University, 2825-7, Huis Ten Bosch, Sasebo, Japan. **Abstrac**---6-Substituted amino-2,4-diaminopyrimidine derivatives were prepared by one-pot synthesis using ketene dithioacetals, amine compounds, and guanidine carbonate in pyridine. These pyrimidine products displayed blue fluorescence in the soli state.
KD-132: Fluorescence-21: Citing: 0.

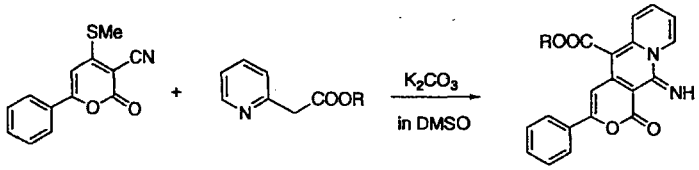



7) **Development of fluorescent 2-pyrone derivatives using ketene dithioacetals for organic EL devices.** Hagimori, Masayori; Mizuyama, Naoko; Shigemitsu, Yasuhiro; Wang, Bo-Cheng; Tominaga, Yoshinori. Faculty of Pharmaceutical Sciences of Nagasaki International University, 2825-7, Huis Ten Bosch, Sasebo, Japan. *Heterocycles* (2009),78(3), 555-570. Publisher: Japan Institute of Heterocyclic Chemistry, CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. AN 2009:299636 CAPLUS **Abstrac**---In recent years, org. electro luminescent (EL) materials have received considerable attention due to their potential application in next-generation display devices with high brightness levels, wide color ranges, and wide viewing angles. Fluorescent 2-pyrone derivs. have been synthesized using a convenient method involving ketene dithioacetals, which emit fluorescence (red, green, and blue) in both soln. (dichloromethane and ethanol) and solid state. The structure-activity relationships of various 2-pyrone derivs. have been clarified.
KD-131: Fluorescence-20: Citing 2.

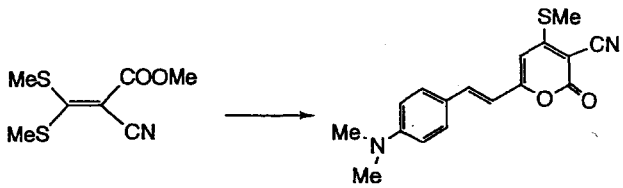



8) **Studies on fluorescence of ionic polyurethane elastomers containing low molecular weight organic dyes.** Nakatani, Takatoshi; Tominaga, Yoshinori; Hiraoka, Kyoko. *Nippon Gomu Kyokaishi* (2008), **81**(6), 197-203. CODEN: NGOKAF ISSN:0029-022X. AN 2008:1055597 CAPLUS. **Abstract**---Thermosetting ionic polyurethane elastomers (IPUEs) contg. sodium sulfonate groups and low mol. wt. org. dyes such as 6-aryl-2*H*-pyrone derivs. (Py series) were prepd. and their photoluminescent (PL) properties, ionic conductivities and Tg were investigated. PL properties of dyes in the IPUEs were found to be similar to those in dichloro-methane, and some Py dyes showing stronger emission in the IPUEs commonly had *N*,*N*-dimethylamino groups at the 4-position of the aryl rings. For the IPUEs, variance of the ionic group contents did not affect PL properties, but effects of the dye contents on Tg, conductivities and aging behaviors of PL properties were different depending on the dyes used. Since no aging were obsd. for the dyes in the solid state, the aging of the IPUEs was considered to be due to photodegrdn. of the IPUE matrixes. The aging rates of the IPUEs contg. a Py dye showing stronger emission were higher than those of others. In addn., Tg elevation and the decrease of cond. was obsd. by increase of the Py dye content. These results suggested that the Py dye might have considerably strong interaction with the IPUE matrix.
KD-130: Citing 0.

9) **Synthesis of pyrano[4,3-*b*]quinolizine derivatives from 6-aryl or styryl-4-methylsulfanyl-2-oxo-2*H*-pyrans and their fluorescence.** Hagimori, Masayori; Mizuyama, Naoko; Tominaga, Yoshinori. *ARKIVOC* (Gainesville, FL, United States) (2008), (13), 16-27. CODEN: AGFUAR AN 2008:838324 CAPLUS. **Abstract**---New fluorescent compds.1,11-dihydro-11-imino-1-oxo-3-phenylpyrano[4,3-*b*]quinolizines were synthesized in good yields by the reaction of 6-aryl-3-cyano-4-methylsulfanyl-2*H*-pyrones and 4-methylsulfanyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrole-3-carbonitrile with 2-pyridylacetates. These fused quinolizine derivs. exhibited fluorescence in solid and soln. states.
KD-129: Fluorescence-19: Citing 2.



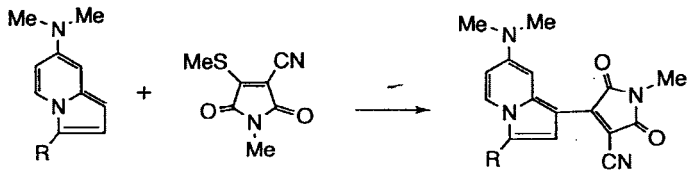

10) **Ketene dithioacetals for organic electroluminescence displays.** Tominaga, Yoshinori; Mizuyama, Naoko; Hagimori, Masayori. *Mirai Zairyo* (2008), **8**(5), 52-61. CODEN: MZIABA ISSN:1346-0986. CAN 149:20865 AN 2008:702809. CAPLUS. **Abstract**---A review on the ketene dithioacetals for org. electrol-uminescence displays.
KD-128: Fluorescence-18: Citing 0.




11) **TD-DFT investigation on the electronic spectra of novel *N*-methylmaleimides linked with indolizine ring system.** Shigemitsu, Yasuhiro; Komiya, Kaori; Mizuyama, Naoko; Tominaga, Yoshinori. *THEOCHEM* (2008), 855(1-3), 92-101. CODEN: THEODJ ISSN:0166-1280. CAN 149:307286. AN 2008:431831 CAPLUS. **Abstract**---The major electronic absorption features in visible region were computationally investigated for a series of novel *N*-methylmaleimide derivs. The newly synthesized compds. through the reaction of indolizines with *N*-methylmaleimides exhibited their maxima ranging 587-634 nm in soln. at room temp. Time dependent d. functional theory (TD-DFT) calcns. were performed in order to elucidate their structure-color relationship, as well as to assess its performance using a variety of

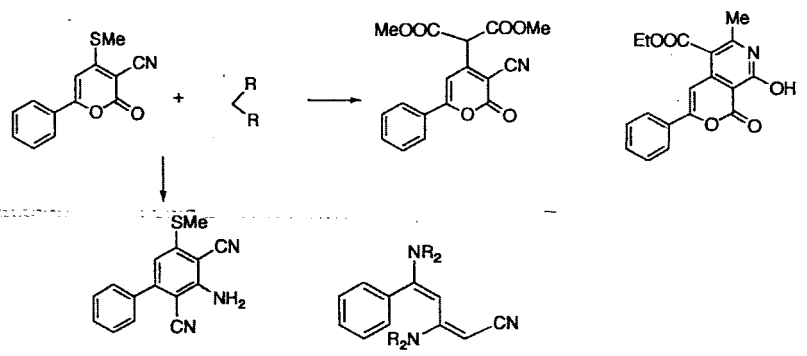
exchange-correlation (XC) functionals and basis sets. 4-(Indolizin-3-yl)-1-methyl-2,5-dioxo-1*H*-pyrrole-3-carbonitrile (referred to 3a hereafter), a representative of the new compds., was analyzed in detail on its intramol. push-pull electronic structure. As a consequence of systematic evaluation of computational strategies for 3a, we found that the theor. λmax obtained by PCM-TD-DFT/6-31+G(d, p)//DFT/6-311G(2d, 2p) level of theory, which was consistently employed throughout this study, has converged within 2 nm deviation from λmax of the most elaborated level considered. Among some of the mols. with near-planarity structure, unusual discrepancies between the theor. and the exptl. λmax were obsd., which should be attributed to the well-known TD-DFT limitation to describe multi-configurational or charge transfer (CT) excitations.

KD-127: Fluorescence 17: Citing 4.



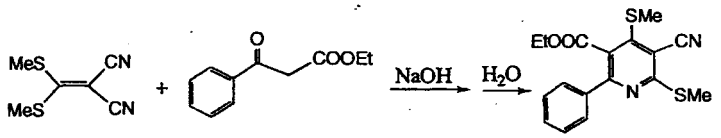
12) **Reaction of 6-aryl- or styryl-4-methylsulfanyl-2-oxo-2*H*-pyrans with active methylene compounds and fluorescence properties of the products.** Mizuyama, Naoko; Murakami, Yuka; Nakatani, Takatoshi; Kuronita, Keiko; Kohra, Shinya; Ueda, Kazuo; Hiraoka, Kyoko; Tominaga, Yoshinori. *Journal of Heterocyclic Chemistry* (2008), 45(1), 265-277. CODEN: JHTCAD ISSN:0022-152X. CAN 148:333381 AN 2008:88695 CAPLUS. **Abstract**--New 2-pyrone derivs., dialkyl 3-cyano-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates and alkyl 3-cyano-6-phenyl-2-oxo-2*H*-pyran-4-ylacetates, which were easily prepd. by the reaction of 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles with active methylene compds. in the presence of potassium carbonate, show fluorescence emission radiation. The light-emitting region of di-Me 3-cyano-6-(4-*N*,*N*-dimethylamino)styryl-2-oxo-2*H*-pyran-4-ylmalonate was 620 nm in dichloromethane, making this compd. a typical red fluorophore. Me 8-hydroxy-6-methyl-1-oxo-3-phenyl-1*H*-pyrano-[3,4-*c*]pyridine-5-carboxylate derivs. also showed fluorescence in the solid state. This is the first example of fluorescence in fused 2-pyrone derivs.

KD-126: Fluoresence-16: Citing 1.

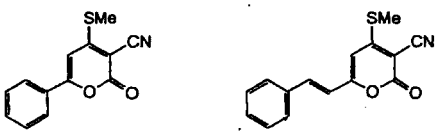


13) **One-pot synthesis of polysubstituted pyridine derivatives using ketene dithioacetals.** Hagimori, Masayori; Mizuyama, Naoko; Hisadome, Yukari; Nagaoka, Junko; Ueda, Kazuo; Tominaga, Yoshinori. *Tetrahedron* (2007), 63(11), 2511-2518. CODEN: TETRAB ISSN:0040-4020. AN 2007:158820 CAPLUS. **Abstract**---Polysubstituted pyridine derivs. were synthesized by the reaction of ketene dithioacetal, 3,3-bis—(methylsulfanyl)methylenemalononitrile 1b, with a variety of active methylene compds. in the presence of either sodium hydroxide or potassium hydroxide as a base in DMSO. This reaction was carried out under economical one-pot reaction conditions (cheap catalyst and solvent) and solved the problem of the odor of methanethiol, commonly derived from reactions of ketene dithioacetals. This is a significant enhancement of GSC (green and sustainable chem.) in the field of ketene dithioacetal chem.

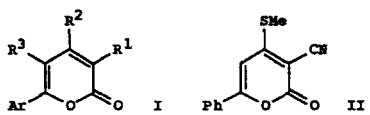
KD-125: Fluorescence-15: Citing 4.



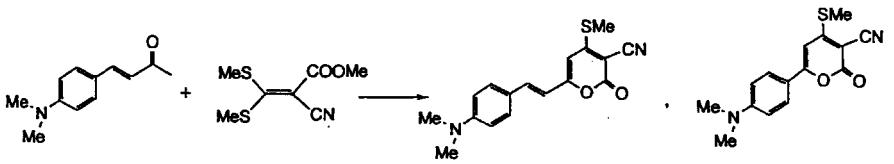
14) **Synthesis and fluorescence of 2*H*-pyrone derivatives for organic light-emitting diodes (OLED).** Mizuyama, Naoko; Murakami, Yuka; Kohra, Shinya; Ueda, Kazuo; Hiraoka, Kyoko; Nagaoka, Junko; Takahashi, Kojiro; Shigemitsu, Yasuhiro; Tominaga, Yoshinori. *Journal of Heterocyclic Chemistry* (2007), **44**(1), 115-132. CODEN: JHTCAD ISSN:0022-152X. AN 2007:147946 CAPLUS. **Abstract**---2*H*-Pyrone derivs. were synthesized through the reaction of aryl acetyl compds. with ketene dithioacetals in the presence of sodium hydroxide, and they showed very strong fluorescence in the solid state. The light-emitting region of these 2*H*-pyrones is 447-630 nm in the solid states.
KD-124: Fluorescence-14: Citing 5.



15) **The organic fluorescent compound, its manufacture, the luminescence agent for organic electroluminescence elements, and the organic electroluminescence element.** Tominaga, Yoshinori; Mizuyama, Naoko; Murakami, Yuka. *Jpn. Kokai Tokkyo Koho* (2006), 48pp. CODEN: JKXXAF JP 2006206523 A 20060810 CAN 145:230532 AN 2006:787662 CAPLUS. **Abstract**---The 6-aryl-2*H*-pyran-2-ones represented by the formula I ($R^1$= electron-withdrawing group; $R^2$ = S, O or N contg. substituent; $R^3$ = H, alkyl or phenyl; Ar = 4-$R^2NC_6H_4$, 4-$R^3C_6H_4CH$=CH- or 4-$R^2NC_6H_4CH$=CH-; R = alkyl or allyl) were prepd. For example, reaction of Me 2-cyano-3,3-bis(methylthio)acrylate with 2-methoxy-acetophenone gave II. I showed remarkable sensitivity to the UV light or the visible ray and remarkable luminescence ability.
KD-123: Fluorescence-13: Citing 2.

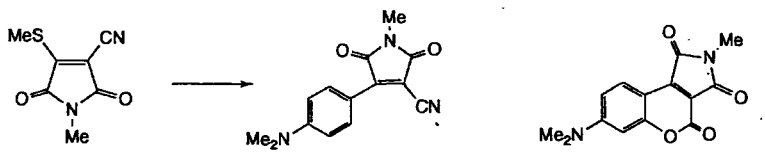


16) **Synthesis and fluorescence of 6-(4-dimethylaminophenyl)- and 6-[2-(4-*N*,*N*-disubstituted aminophenyl)vinyl]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitriles in solution and in the solid states.** Mizuyama, Naoko; Murakami, Yuka; Nagaoka, Junko; Kohra, Shinya; Ueda, Kazuo; Hiraoka, Kyoko; Shigemitsu, Yasuhiro; Tominaga, Yoshinori. *Heterocycles* (2006), **68**(6), 1105-1108. CODEN: HTCYAM ISSN:0385-5414. CAN 145:249046 AN 2006:623166 CAPLUS. **Abstract**——Fluorescent dyes, 6-[4-(dimethyl-amino)phenyl]-4-(methylthio)- and 6-[2-(4-*N*,*N*-disubstituted aminophenyl)vinyl]-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitriles were synthesized by the reaction of 4-(dimethylamino)-acetophenone and 4-aminobenzalacetones with ketene dithioacetal $(MeS)_2C$:$C(CN)CO_2Me$ in the presence of NaOH in DMSO at room temp. These 2-pyrone derivs. showed orange and red fluorescence (Fmax: 607, 699, 705, 645 nm) in $CH_2Cl_2$. The prepn. and fluorescence of 4-amino-2H-pyrone derivs. is also described. The crystal structure of 6-[4-(dimethylamino)phenyl]-4-(dimethylamino)-3-cyano-2*H*-pyrone is presented [orthorhombic, space group P212121, a 7.5938, b 14.0254(), c 27.4606 .ANG., V 2924.72 .ANG.3, Z 8].
KD-122: Fluorescence-12: Citing 5.

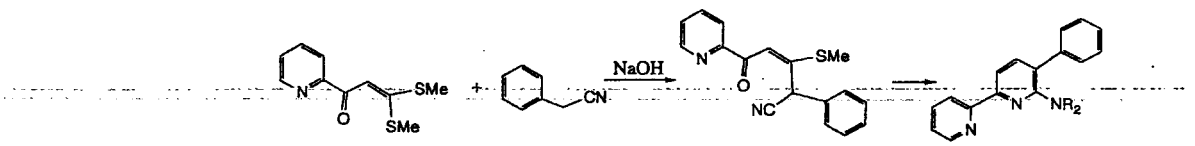


17) **Reaction of functionalized maleimides with versatile nucleophiles. Synthesis, electronic spectra and molecular orbital study.** Shigemitsu, Yasuhiro; Komiya, Kaori; Mizuyama, Naoko; Tominaga, Yoshinori. *Dyes and Pigments* (2006), Volume Date 2007, 72(3), 271-284. CODEN: DYPIDX ISSN:0143-7208. AN

2006:598487 CAPLU. **Abstract**——This article comprehensively describes the condensation reactions of functionalized maleimides (3-methylthio-2,5-dioxo-1*H*-pyrroles) with some nucleophilic reagents to afford a series of novel heterocycles, as briefly reported in a previous communication [Tominaga Y, Komiya K, Itonaga S, Yoshioka N, Kataoka S, Sasaki K, et al. Heterocycles 1997;46:41]. The reactions of the functionalized maleimides (5a-c) with *N,N*-dialkylanilines (6a-d) smoothly proceeded to give the corresponding 3-(4-dialkylamino)phenyl-1-methyl-1*H*-pyrrole-2,5-diones (7a-i). Cyclic products, the 2*H*,4*H*-[1]benzopyrano[3,4-*c*]pyrrole-1,3,4-triones (10a-c, 12, 13) were also obtained within the same reaction framework, using 3-dialkylaminophenols (6g-j) and resorcinol (6k) as the nucleophilic reagents. Further treatments of (7a,b,h) with Lawesson's reagent afforded the brilliant blue mono-thiocarbonyls, 4-(4-dialkylamino)phenyl-3-cyano-1-methyl-5-oxo-pyrrole-2-thiones (9a-c). The UV/vis spectral characteristics of the new heterocycles, particularly of the controversial arom. mono-thiocarbonyl compds. (9a-c), were computationally analyzed by means of semi-empirical and Time Dependent D. Functional Theory (TDDFT) quantum chem. calcns.
KD-121: Fluorescence-11: Citing 3.



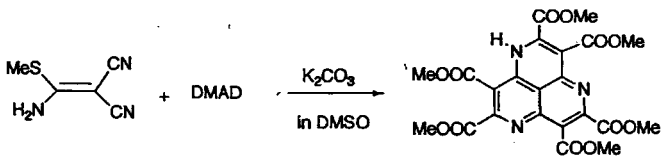

18) **Synthesis and steady-state spectroscopic study of 5-aryl-2,2'-bipyridyls. New fluorescent compounds in solid state.** Mizuyama, Naoko; Tominaga, Yoshinori; Kohra, Shinya; Ueda, Kazuo; Hirayama, Shun-ichi; Shigemitsu, Yasuhiro. *Bulletin of the Chemical Society of Japan* (2006), 79(4), 602-611. CODEN: BCSJA8 ISSN:0009-2673. CAN 145:103509 AN 2006:434551 CAPLUS. **Abstract**——The absorption and fluorescent properties of newly synthesized 5-aryl-2,2'-bipyridyls were examd. both in soln. and in the solid state. The 6-methoxy derivs. have weak fluorescence, whereas 6-amino derivs. showed strong fluorescence. Their spectroscopic properties were computationally analyzed using semi-empirical MO calcns. The geometries of the ground (S0) and the first singlet excitation states (S1) were optimized and employed to est. the vertical transition energies. The drastic differences in fluorescent intensities between the methoxy and amino derivs. can be qual. explained by the relative energy levels S1 and the neighboring triplet level; the energy gaps supposedly regulate the non-radiative intersystem crossing (ISC) probabilities. On the relaxed S1 geometry, the methoxy compds. have quite small S1-triplet energy gaps, whereas the amino derivs. have no such quasi-degeneracies, leading to their quant. different quantum yields.
KD-120: Fluorescence-10: Citing 5.




19) **Theoretical molecular design of photofunctional organic compounds by means of material simulation. Quantum chemical calculation of synthesis and fluorescent property of novel heterocyclic compounds** Shigemitsu, Yasuhiro; Hirayama, Shun-ichi; Tominaga, Yoshinori. *Nagasaki-ken Kogyo Gijutsu Senta Kenkyu Hokoku* (2005), Volume Date 2004, 34, 55-59. CODEN: NGSHEU ISSN:0916-6726. CAN 145:27420 AN 2005:1257309 CAPLUS. **Abstract**——In an attempt to obtain photofunctionally versatile org. compds., 8 5-aryl[2,2']bipyridyl derivs. were synthesized from α-oxodiketene dithioacetals and phenylacetonitriles and evaluated by quantum chem. calcn. The fluorescent intensities in the soln. and solid states were quant. analyzed and discussed by using semiempirical MO method (AMI-SDCI).
KD-119: Citing-0.

20) **Synthesis of dimethyl heterocyclic-*o*-dicarboxylates using dimethyl acetylenedicarboxylate.** Tominaga, Yoshinori; Ueda, Kazuo. *Journal of Heterocyclic Chemistry* (2005), 42(3), 337-352. CODEN: JHTCAD ISSN:0022-152X. CAN 143:59854 AN 2005:369792 CAPLUS. **Abstract**——A review. Di-Me acetylenedicarboxylate (DMAD) is a very important and useful reagent for the prepn. of di-Me heterocyclic-*o*-dicarboxylates, which are key intermediates in the synthesis of fused pyridazine derivs. The synthesis of thiopyrans by the Diels-Alder reaction of dithiocarboxylate derivs., synthesis of various cyclazines by [2 + 8] cycloaddn. reactions, and synthesis of di-Me pyrazolo[3,4-*b*]pyridine-5,6-di-

carboxylates and polycyclic heterocycles contg. the 1,6-naphthyridine ring system by the reaction of o-aminonitrile compds. with DMAD are described here.
KD-118: Citing 11.

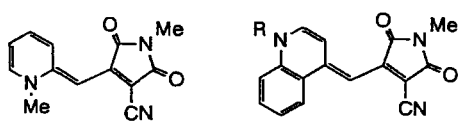



21) **Winter cherry bugs feed on plant tropane alkaloids and de-epoxidize scopolamine to atropine** Kitamura, Yoshie; Tominaga, Yoshinori; Ikenaga, Toshihiko. *Journal of Chemical Ecology* (2004), **30**(10), 2085-2090. CODEN: JCECD8 ISSN:0098-0331. CAN 142:173589 AN 2004:880321 CAPLUS. **Abstract**---- The winter cherry bug colonizes the Duboisia leichhardtii tree, which is a rich source of scopolamine. It consumes the tropane alkaloids atropine and scopolamine. Quant. anal. revealed that the ratio of scopolamine to atropine in the winter cherry bug (0.46) was far from that found in the leaves of the host plant (7.20). To elucidate whether the winter cherry bugs selectively excrete or decomp. scopolamine, they were fed scopolamine and/or atropine together with sucrose. They took up scopolamine as well as atropine, and converted scopolamine into atropine.

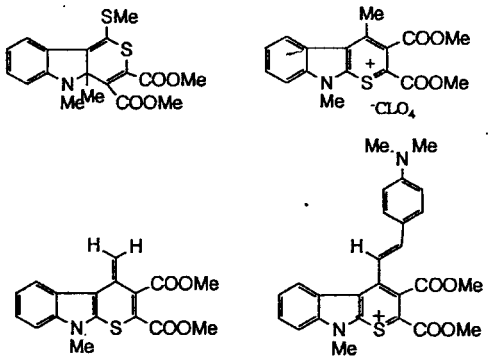
22) **Product class 7: cyclazines** Tominaga, Y. *Science of Synthesis* (2004), **17**, 1025-1079. CODEN: SSCYJ9 CAN 142:93703 AN 2004:202761 CAPLUS.. **Abstract**---A review. Methods for prepg. cyclazines are reviewed including cyclization, substituent modification, and aromatization. Review.
KD-117: Citing 1.


23) **Molecular design of photofunctional organic compounds by material simulation method and quantum chemical analysis of [2.2.3]cyclazine.** Shigemitsu, Yasuhiro; Hirayama, Shunichi; Tominaga, Yoshinori. *Nagasaki-ken Kogyo Gijutsu Senta Kenkyu Hokoku* (2004), Volume Date 2003, **32**, 57-61. CODEN: NGSHEU ISSN:0916-6726. CAN 143:59352 AN 2004:794834 CAPLUS. **Abstract**---Quantum chem. anal. of photofunctional [2.2.3]cyclazine was carried out by applying complete active space self consistent field/2nd order CAS perturbation theory (CASSCF/CASPT2). Based on calcn., the ground and low excited states of valence electrons in the compd. were analyzed and their electron spectrum peaks were identified. Empirical values for 3 main peaks were in accordance with the calcd. ones in the UV/VIS spectrum.
Citing 1.

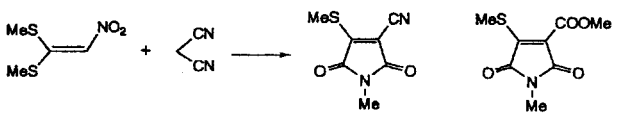
24) **Synthesis and electronic spectra of novel merocyanine dyes bearing a maleimide ring incorporated into the methine chains.** Shigemitsu, Yasuhiro; Sugimoto, Manabu; Itonaga, Sachiko; Komiya, Kaori; Tominaga, Yoshinori. *Dyes and Pigments* (2003), **56**(2), 167-179. CODEN: DYPIDX ISSN:0143-7208. CAN 138:305528 AN 2002:980038 CAPLUS. **Abstract**----The present article describes the synthesis of new polymethine dyes with a heterocyclic ring incorporated into the methine chain. 1-Alkyl-2- or 4-methylpyridinium salts and related compds. reacted at the exocyclic double bond with cyano- or methoxycarbonyl heterocycles bearing a methylthio group to give new polymethine dyes in good yield. This reaction occurred by an addn.-elimination mechanism, involving nucleophilic attack of cyclic enamines at deficient carbon atoms on the heterocycles followed by elimination of MeSH. The polymethine dyes obtained are red, violet, and blue in color with absorption peaks at 524-614 nm. Semi-empirical as well as ab-initio quantum chem. calcns. were used to theor. characterize their $\pi$-$\pi$ absorption maxima in the visible region which plays a decisive role in their color appearances.
KD-116: Citing 6.



25) **Synthesis of new thiopyrylocyanines incorporating a thiopyrano[2,3-*b*]indole ring as the main constituent.** Tominaga, Yoshinori; Shigemitsu, Yasuhiro; Hirayama, Shun-ichi. *Heterocycles* (2002), 57(12), 2227-2230. CODEN: HTCYAM ISSN:0385-5414. CAN 138:353852 AN 2002:955143 CAPLUS. **Abstract**----The Diels-Alder product, di-Me 4a,5-dimethyl-1-(methylthio)thiopyrano[4,3-*b*]indole-3,4-di-carboxylate (I), which was obtained by reaction of Me 1,2-dimethylindole-3-dithiocarboxylate with di-Me acetylenedicarboxylate, was easily converted to a 1,5-dimethyl-2,3-bis(methoxycarbonyl)indolo[2,3-*b*]-thio-pyrylium perchlorate (II) as the key intermediate for thiopyrylocyanine and merocyanine dyes. Compds. II and III were allowed to react with arom. aldehydes and some electrophilic reagents to yield cyanine and merocyanine dyes, e.g., IV (R = Me, Et), in good yields.
CS-49: Citing 2.



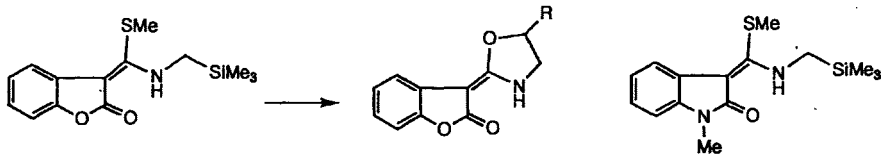
26) **Synthesis of methylthiomaleimides for the preparation of pyridazines and related compounds.** Tominaga, Yoshinori; Shigemitsu, Yasuhiro; Sasaki, Kenji. *Journal of Heterocyclic Chemistry* (2002), 39(3), 571-591. CODEN: JHTCAD ISSN:0022-152X. CAN 137:385991 AN 2002:508215 CAPLUS. **Abstract**----New functionalized maleimides [3-(methylthio)-2,5-dioxo-1*H*-pyrroles] were obtained by the reaction of ketene dithioacetals with nitromethane or the reaction of nitro ketene dithioacetal with active methylene compds. in the presence of the appropriate base in DMSO followed by treatment with methanol. These maleimides reacted with various nucleophilic reagents such as electron-rich arom. and heteroarom. compds. like dialkylanilines, aminophenols, indoles, indolizines, and cyclazines to give the corresponding 3-aryl- or -heteroaryl-1*H*-pyrrole-2,5-diones. Styryl and merocyanine dyes, and polycyclic pyridazinediones as chemiluminophors and succinimides were also obtained from these maleimides with good results.
KD-115: Citing 11.



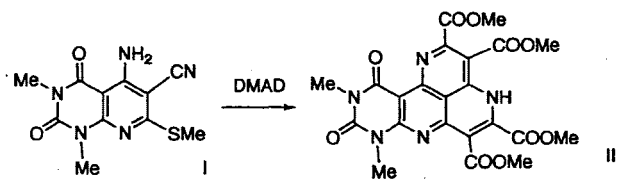
27) **Development of novel functional dye using computed-aided molecular design techniques and its application to reagents for clinical test, etc.** Shigemitsu, Yasuhiro; Tominaga, Yoshinori; Hirayama, Shunichi. *Nagasaki-ken Kogyo Gijutsu Senta Kenkyu Hokoku* (2001), Volume Date 2000, **29**, 23-33. CODEN: NGSHEU ISSN:0916-6726. CAN 136:201769 AN 2001:806768 CAPLUS. **Abstract**—Novel functional cyanine/merocyanine dyes were synthesized using versatile reactivity of nucleophilic reagents, ketenedithioacetals and 4-methylthiomaleimides. Quantum chem. calcns. based on the MO method were carried out for light absorption anal. of these dyes. Also, absorption spectra of photochromic spirooxazine compds. showing absorptions in the longer wavelength region were theor. analyzed aiming at the mol. design of new photochromic compds.

28) **Synthesis and [3+2] cycloaddition reaction of 3-[(trimethylsilylmethylamino)(methylthio)-methylene]-heterocyclic compounds.** Tominaga, Yoshinori; Takada, Satoshi; Kohra, Shinya; Shigemitsu, Yasumitsu. *Journal of Heterocyclic Chemistry* (2001), 38(5), 1143-1151. CODEN: JHTCAD ISSN:0022-152X. CAN 136: 183744 AN 2001:779594 CAPLUS. **Abstract**----3-[(Trimethyl-silylmethylamino)(methylthio)] methyl-ene-2- coumaranone (4a) and -1-methyloxindole (4b), readily prepd. by reactions of the corresponding bis(methylthio)methylene heterocyclic compds. with (trimethylsilyl- methyl)amine, are the synthetic equiv. of heterocyclic alkylideneazomethine ylides. Reactions of 4a, b with reactive heterodipolarophiles such as

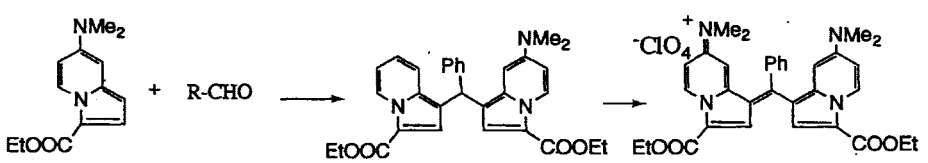
aldehydes and ketones and reactive alkenes in the presence of CsF gave the 1,3-dipolar cycloadducts, 3-(2-oxazolidinylidene)-oxindole and -coumaran-2-one derivs., as well as pyrrolylidenecoumaran-2-one and oxindole derivs., via the 1,3-elimination of (methylthio)trimethylsilane.
KD-114: Citing 0.



29) **Synthesis of polycyclic nitrogen-containing heterocyclic [1]: one pot formation of 1,6-naphthyridine ring system by reaction of amino-cyano-methylthio-heterocycles with dialkyl acetylenedicarboxylates.** Tominaga, Yoshinori; Nomoto, Kenichi; Yoshioka, Noriko. *Journal of Heterocyclic Chemistry* (2001), **38**(5), 1135-1141. CODEN: JHTCAD ISSN:0022-152X. CAN 136:167348 AN 2001:779593 CAPLUS. **Abstract**——Reaction of 3-amino-3-methylthio-2-cyanoacrylonitrile [[amino(methylthio)methylene]-propanedinitrile] with excess di-Me acetylenedicarboxylate(DMAD) in the presence of potassium carbonate in DMSO gave a novel tricyclic heterocycle, hexamethyl 1*H*-1,4,7-triazaphenalene-2,3,5,6,8,9-hexacarboxylate [I; 1*H*-pyrido[2,3,4-*de*][1,6]naphthyridine-2,3,5,6,8,9-hexacarboxylic acid hexamethyl ester]. When one equiv. of DMAD was used in this reaction, 4-amino-5-cyano-6-(methylthio)-2,3-pyridine-dicarboxylic acid di-Me ester, a key intermediate of I, was obtained. The compds. thus prepd. included derivs. of 1*H*-pyrimido[4,5,6-*de*][1,6]naphthyridine, 1*H*-[1,2,4]triazolo[1',5':1,2]pyrimido[4,5,6-*de*][1,6]-naphthyridine, 4*H*-pyrazolo[1',5':1,2]pyrimido[4,5,6-*de*][1,6]naphthyridine, 4*H*-pyrazolo-[1',5':1,6]pyrido-[4,3,2-*de*][1,6]naphthyridine and 4*H*-pyrido[2,3,4-de]pyrimido[4,5-*b*][1,6]naphthyridine.
KD-113: Citing 3.

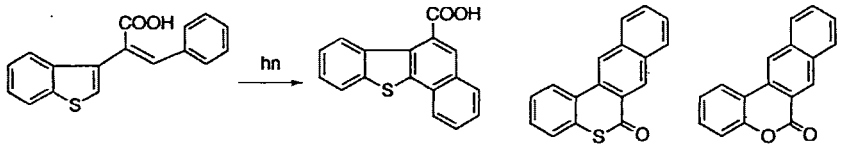


30) **Synthesis of bis(7-dimethylamino-1-indolizinyl)methane derivatives and their oxidation: as an oxidative chromogenic reagent in clinical analysis.** Tominaga, Yoshinori; Itonaga, Sachiko; Kouno, Tetsuya; Shigemitsu, Yasuhiro. *Heterocycles* (2001), **55**(8), 1447-1450. CODEN: HTCYAM ISSN: 0385-5414. CAN 135:344341 AN 2001:599467. CAPLUS. **Abstract**——Acid-catalyzed condensation of 7-(dimethylamino)-3-indolizinecarboxylic acid Et ester and 7-(dimethylamino)-2-(methylthio)-3- indolizine-carboxylic acid Et ester with aldehydes gave substituted bis(7-dimethylaminoindolizin- 1-yl)methanes which were easily converted into substituted bis(7-dimethylaminoindolizin-1-yl)methyl cations by oxidn. with DDQ. These triaryl cation dyes were converted to the new heterocyclic ring system, 12-dimethylamino-6,8-bis(ethoxycarbonyl)-2*H*-thiopyrano[3,2-*a*:5,6-*a*']diindolizine-2-*N*,*N*-dimethylaminium perchlorates, under reflux conditions in ethanol.
KD-112: Citing 3.

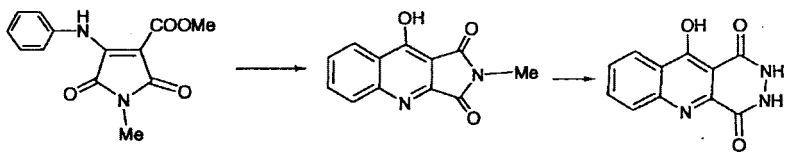


31) **Synthesis of thiopyrone and pyrone derivatives by photocyclization reaction of 3-aryl-2-([1]benzothien-3-yl)propenoic acids.** Sasaki, Kenji; Satoh, Yasuyoshi; Hirota, Takashi; Nakayama, Taiji; Tominaga, Yoshinori; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (2000), **37**(4), 959-967. CODEN: JHTCAD ISSN:0022-152X. CAN 134:17374 AN 2000:708008 CAPLUS **Abstract**-----Naphtho-[1,2-*b*][1]benzothiophene-6-carboxylic acids, 6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-ones and 6*H*-benzo[*b*]-naphtho[2,3-*d*]pyran-6-ones were synthesized in one step by the photocyclization reaction of 3-aryl-2-([1]benzothien-3-yl)propenoic acids. The photocyclization reaction did not occur when the 3-aryl group contained the electron-withdrawing nitro group. The assignment of the $^{1}H$ and $^{13}C$ NMR spectra of

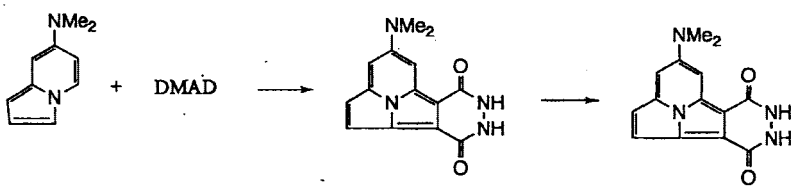
6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one and 6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one by two-dimensional NMR methods is described. The difference between the chem. shift values of H12 for these two compds. is attributed to different mol. geometries.
Thiophene-19: Citing 3.




32) **Synthesis and chemiluminescence of 10-hydroxy- and 10-aminopyridazino[4,5-*b*]quinoline-1,4(2*H*, 3*H*)-diones.** Tominaga, Yoshinori; Yoshioka, Noriko; Kataoka, Seigo; Shigemitsub, Yasuhiro; Hirota, Takashi; Sasaki, Kenji.*Heterocycles* (1999), **50**(1), 43-46. CODEN: HTCYAM ISSN:0385-5414. CAN 130:182424 AN 1999:29299 CAPLUS **Abstract**-----Substituted anilines $RC_6H_4NH_2$ [R = H, 3-MeO, 4-MeO, 3,4-$(MeO)_2$, 4-$Et_2N$] reacted with Me 1-methyl-4-methylthio-2,5-dioxo-3-pyrroline-3-carboxylate in refluxing methanol to give the corresponding Me 1-methyl-2,5-dioxo-4-phenylamino-3-pyrroline-3-carboxylates I which were converted in good yields to 2-methylpyrrolo[3,4-*b*]quinoline derivs. II by heating in di-Ph ether. Reaction of II with hydrazine hydrate gave 10-hydroxypyridazino[4,5-*b*]quinoline-1,4(2*H*,3*H*)-diones III (X = OH) in good yields. The desired 10-aminopyridazino[4,5-*b*]-quinoline-1,4(2*H*,3*H*)-diones III (X = $NH_2$) were obtained by the chlorination of II with phosphorus oxychloride followed by ammonolysis with 28% ammonium hydroxide in good yields. Compds. III were found to be efficiently chemiluminescent in a similarly to luminol in the presence of $H_2O_2$ and horseradish peroxidase in a soln. of a phosphate buffer pH 8.0.
KD-111: Fluorescence 9: Citing 7.

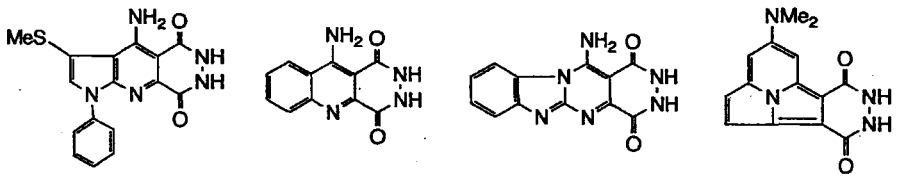



33) **Synthesis of a luminescent compound: 8-dimethylaminopyridazino[4,5-*a*][2.2.3]cyclazine-1,4(2*H*,3*H*)-diones.** Tominaga, Yoshinori; Komiya, Kaori; Kataoka, Seigo; Shigemitsu, Yasuhiro; Hirota, Takashi; Sasaki, Kenji. *Heterocycles* (1998), **48**(10), 1985-1988. CODEN: HTCYAM ISSN:0385-5414. CAN 130:110224 AN 1998:779058 CAPLUS. **Abstract**----Some chemiluminescent pyridazino[4,5-*a*] [2.2.3]-cyclazine-1,4(2*H*,3*H*)-diones were synthesized via several steps from indolizine derivs. The key intermediates, di-Me 6-dimethylamino[2.2.3]cyclazine-1,2-dicarboxylates were synthesized by the [8+2] cycloaddn. reaction of 7-dimethylaminoindolizines with di-Me acetylenedicarboxylate in the presence of Pd-C in refluxing toluene.
KD-110: Fluorescence 8: Citing 8.

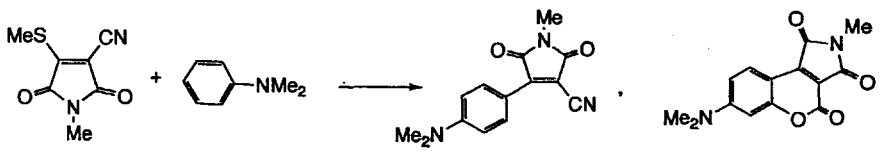



34) **Synthesis of polycyclic pyridazinediones as chemiluminescent compounds.** Tominaga, Yoshinori; Sasaki, Kenji; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1998), **35**(5), 1219-1235. CODEN: JHTCAD ISSN:0022-152X. CAN 130:66414 AN 1998:725610 CAPLUS. **Abstract**----Review with >23 refs. Reactions of 1,3-disubstituted 5-aminopyrazole-4-carbonitrile derivs. with di-Me acetylene- dicarboxylate in the presence of potassium carbonate in DMSO gave di-Me 1,3-disubstituted pyrazolo-[3,4-*b*]pyridine-5,6-dicarboxylates (I) which were allowed to react with excess hydrazine hydrate under ethanol refluxing conditions followed by heating at 250-300°C to give 1,3-disubstituted 4-amino-1*H*-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazine-5,8(6*H*,7H)-diones in good yields. Similarly, 1,3-disubstituted 4-hydroxy-1*H*-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazine-5,8(6*H*,7*H*)-diones were obtained from alkyl 1,3-di-substituted 5-aminopyrazole-4-carboxylates. These tricyclic pyridazine derivs. were alternatively

synthesized from 4-hydroxypyrrolo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5,7-diones prepd. by reactions of 5-amino-pyrazoles with Me 1-methyl-4-methylthio-2,5-dioxo-1*H*-pyrrole-3-carboxylate, followed by the Gould/Jacobs reaction. 1-Methyl-4-methylthio-2,5-dioxo-1*H*-pyrrole-3-carbonitrile smoothly reacted with 2-aminobenzimidazoles to give 5-amino-3-methyl-1*H*-pyrrolo[3',4':4,5]pyrimido[1,2-*a*]benzimidazole-1,3-(2*H*)-diones, which were readily converted to 12-aminopyridazino[4',5':4,5]- pyrimido[1,2-*a*]benz-imidazole-1,4(2*H*,3*H*)-diones in good yields. Other pyridazinopyrimidine derivs. were also obtained by the reaction of 2-aminoheterocycles with the maleimide in good yields. Substituted anilines reacted with 1-methyl-4-methylthio-2,5-dioxo-1*H*-pyrrole-3-carbonitrile in refluxing methanol to give Me 4-phenyl-amino-1-methyl-2,5-dioxo-1*H*-pyrrole-3-carboxylates which were converted in good yields to 2-methyl-pyrrolo[3,4-*b*]quinoline derivs. by heating in di-Ph ether. Reaction of these compds. with hydrazine hydrate gave 10-hydroxypyridazino[4,5-*b*]quinoline-1,4(2*H*,3*H*)-diones in good yields. The desired 10-amino-pyridazino[4,5-*b*]pyridazine-1,4(2*H*,3*H*)-diones were obtained in good yields by the chlorination of I with phosphorus oxychloride followed by aminolysis with 28% ammonium hydroxide. Some pyridazino-[4,5-*a*][2.2.3]cyclazine-1,4(2*H*,3*H*)-diones as luminescent compds. were synthesized via several steps from indolizine derivs. The key intermediates, di-Me 6-dimethylamino[2.2.3]cyclazine- 1,2-dicarboxylates, were synthesized by the [8+2] cycloaddn. reaction of 7-dimethylaminoindolizines with di-Me acetylenedi-carboxylate in the presence of Pd-C in refluxing toluene. Some were more efficient than luminol in light prodn. 4-Amino-3-methylsufonyl-1-phenyl-1*H*-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazine- 5,8(6*H*,7*H*)-dione, 10-hydroxypyridazino[4,5-*b*]quinoline-1,4(2*H*,3*H*)-diones, and 10-aminopyridazino[4,5-*b*]quinoline-1,4(2*H*, 3*H*)diones showed the greatest chemiluminescence intensity in the presence of hydrogen peroxide peroxidase in a soln. of phosphate buffer at pH 8.0.
KD-109: Fluorescence 7: Citing 10.

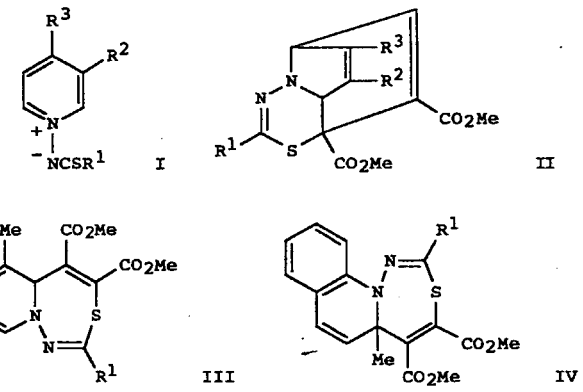


35) **Synthesis of new methine class of dyes bearing maleimide ring system.** Tominaga, Yoshinori; Komiya, Kaori; Itonaga, Sachiko; Yoshioka, Noriko; Kataoka, Seigo; Sasaki, Kenji; Hirota, Takashi. *Heterocycles* (1997), **46** 41-44. CODEN: HTCYAM ISSN:0385-5414. CAN 128:258423 AN 1998:190743 CAPLU. **Abstract**----Condensation of 1-methyl-3-(methylthio)maleimides with *N,N*-dialkylanilines in refluxing acetic acid gave the corresponding 3-[4-(dialkylamino)phenyl]-1- methylmaleimides. Treatment of 2 of these 1-methyl-3-phenylmaleimides with Lawesson's reagent in refluxing toluene afforded 4-[4-(dialkyl-amino)phenyl]-3-cyano-1-methyl-5-oxopyrrole-2-thiones which are brilliant blue dyes with λmax at 606 and 615 nm (log ε: 4.59 and 4.50) in their UV spectra. Reaction of 4-(methoxycarbonyl)-1-methyl-3-(methylthio)maleimide with 3-(dialkylamino)phenols under the same reaction conditions gave cyclized products, 2*H*,4*H*-[1] benzopyrano[3,4-*c*]pyrrole-1,3,4-triones in good yields.
KD-108: Citing 6.

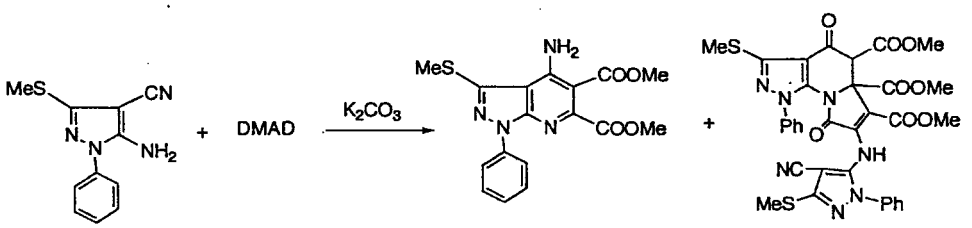


36) **Preparation of New Nitrogen-Bridged Heterocycles. 43. Synthesis and Reaction of 5a*H*-Pyrido-[1,2-*d*][1,3,4]thiadiazepine Derivatives.** Kakehi, Akikazu; Ito, Suketaka; Ishida, Fumihito; Tominaga, Yoshinori. *Journal of Organic Chemistry* (1997), **62**(22), 7788-7793. CODEN: JOCEAH ISSN:0022-3263. CAN 127:307368 AN 1997:658541 CAPLUS. **Abstract**----Reactions of some 1-pyridinio- and 1-(4-methyl-pyridinio)(arenethiocarbonyl)amidates, e.g., I [$R^1$ = 2-thienyl, (un)substituted phenyl; $R^2$, $R^3$ = H, Me] with di-Me acetylenedicarboxylate in chloroform afforded neither the expected di-Me 2-aryl-5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylates nor their intramol. Diels-Alder adducts, but gave novel rearranged products, di-Me 4-aryl-5-thia-2,3-diazatricyclo[4.3.2.02,7]undeca-3,8,10-triene-6,11-di-carboxylates (II) in low to moderate yields. On the other hand, similar reactions of 1-(3-methylpyridinio)- and 1-(2-methylquinolinio)(arenethiocarbonyl)amidates with the same reagent provided 1:1 primary adducts, di-Me 2-aryl-6-methyl-5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylates (III) and di-Me 2-aryl-5a-

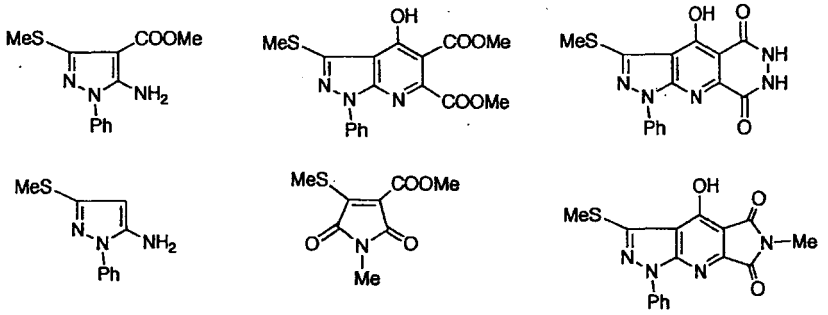
methyl-5a*H*-[1,3,4]thiadiazepino[4,5-*a*]quinoline-4,5- dicarboxylates (IV), resp.
Citing 6.



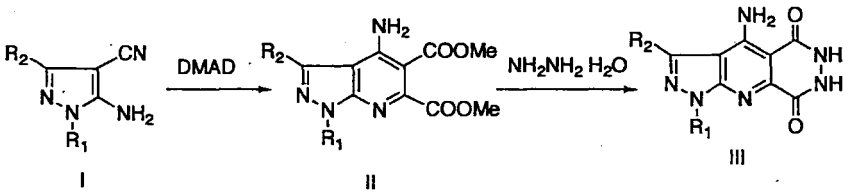
37) **Reaction of 5-amino-1-phenylpyrazole-4-carbonitriles with dimethyl acetylenedicarboxylate. Synthesis and structural determination of trimethyl 4,8-dioxo-1-phenyl-4,5,5a,8-tetrahydro-1*H*-pyrazolo-[3,4-e]indolizine-5,5a,6-tricarboxylate derivatives.** Tominaga, Yoshinori; Yoshioka, Noriko; Castle, Raymond N.; Luo, Jiann-Kuan; Hata, Tadashi. *Journal of Heterocyclic Chemistry* (1997), 34(2), 613-620. CODEN: JHTCAD ISSN:0022-152X. CAN 127:50582 AN 1997:325421 CAPLUS. **Abstract**-----The reaction of 5-amino-1-phenylpyrazole-4-carbonitriles with di-Me acetylenedicarboxylate in the presence of potassium carbonate in DMSO gave tri-Me 4,5,5a,8-tetrahydro-1-phenyl-4,8-dioxo-1*H*-pyrazolo-[3,4-*e*]indolizine-5,5a,6-tricarboxylate derivs. from the basic soln. The products were formed by a double Michael reaction, followed by cyclization to the cyano group.
KD-107: Citing 3.



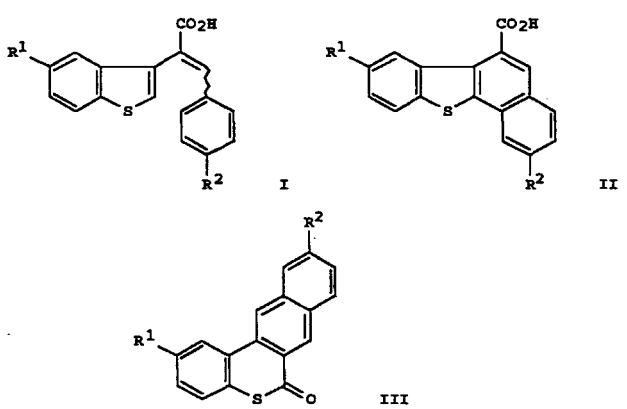
38) **Synthesis and chemiluminescence of 1,3-disubstituted 4-hydroxypyrazolo[4',3':5,6]pyrido[2,3-*d*]-pyridazine-5,8(6*H*,7*H*)-diones.** Tominaga, Yoshinori; Yoshioka, Noriko; Minematsu, Hiroki; Kataoka, Seigo. *Heterocycles* (1997), 44, 85-88. CODEN: HTCYAM ISSN:0385-5414. CAN 126:199489 AN 1997:81970 CAPLUS. **Abstract**----Reactions of 1,3-disubstituted 5-aminopyrazole-4-carboxylate derivs. I ($R^1$ = $SO_2C_6H_4Me$-4, $R^2$ = H, $R^3$ = Et; $R^1$ = $SO_2C_6H_4Me$-4, Ph, $R^2$ = MeS, $R^3$ = Me) with di-Me acetylene-dicarboxylate gave the corresponding di-Me 1,3-disubstituted 4-hydroxypyrazolo[3,4-*b*] pyridine-5,6-di-carboxylates II which reacted with hydrazine hydrate to give 1,3-disubstituted 4-hydroxy-1*H*-pyrazolo-[4',3':5,6]pyrido[2,3-*d*]pyridazine-5,8(6*H*,7*H*)-diones III. These tricyclic pyridazine derivs. were alternatively synthesized from 4-hydroxypyrrolo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5,7-diones IV prepd. by reactions of 5-aminopyrazoles V with 1-methyl-3-methylthio-4-(methoxycarbonyl)maleimide followed by Gould-Jacacobs reaction. These tricyclic pyrazine derivs. were evaluated for chemi- luminescence. 4-Hydroxy-3-methylthio-1-phenyl-1*H*-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazine-5,8- (6*H*,7*H*)-dione showed the greatest chemiluminescence intensity in the presence of $H_2O_2$ and peroxidase in a soln. of phosphate buffer at pH 10.
KD-106: Fluorescence 6: Citing 8.



39) **Method of quantitative determination of peroxide, a peroxidation-active substance or a pyrazolopyridopyridazine derivative.** Tominaga, Yoshinori; Aoyama, Norihito; Masunari, Toshiyuki; Miike, Akira. *Eur. Pat. Appl.* (1996), 18 pp. CODEN: EPXXDW EP 745684 A1 19961204 CAN 126:57100 AN 1997:26437 CAPLUS. **Abstract**-----Disclosed is a chemiluminescent method of quant. detg. one of peroxide (e.g., $H_2O_2$), a peroxidn.-active substance (e.g., peroxidase), or a pyrazolopyrido-pyridazine deriv. represented by I (where $R^1$ represents H, lower alkyl, optionally substituted aryl, optionally substituted heterocyclic group, substituted sulfonyl, substituted sulfinyl, substituted thio, etc.; $R^2$ represents H, lower alkyl, optionally substituted aryl, etc., or a salt thereof), characterized by subjecting an unknown amt. of one substance selected from the peroxide, peroxidn.-active substance, and pyrazolopyridopyridazine deriv. to react with a known amt. of the remaining 2 substances.
KD-105: Fluorescence 5: Citing 5.

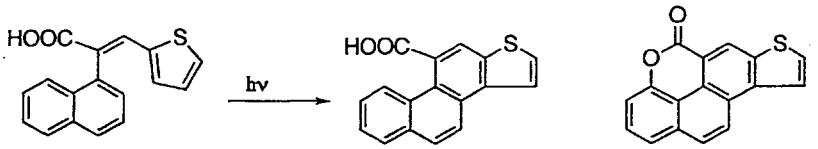


40) **Photocyclization of 2-([1]benzothien-3-yl)-3-phenylpropenoic acids.** Tominaga, Yoshinori; Castle, Lyle W.; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1996), 33(4), 1319-1321. CODEN: JHTCAD ISSN:0022-152X. CAN 125:300701 AN 1996:582779 CAPLUS. **Abstract**---- Photocyclization of the substituted 2-([1]benzothien-3-yl)-3-phenylpropenoic acids I ($R^1 = R^2 = H$; $R^1$ = Me, R2 = H, OMe) in the presence of iodine and air in a benzene-cyclohexane mixt. afforded a separable mixt. of three compds., benzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic acids II, 6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-ones III, and 10-methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one.
Thiophene-20: Citing 5.

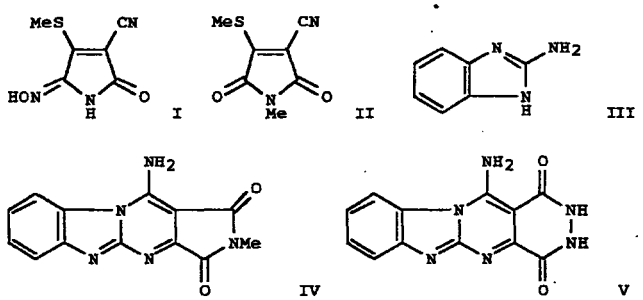


41) **Photocyclization of 2-(naphth-1-yl)-3-(thien-2-yl)propenoic acid and the total assignment of the $^1$H- and $^{13}$C-NMR spectra of the product.** Tominaga, Yoshinori; Castle, Lyle W.; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1996), 33(4), 1017-1018. CODEN: JHTCAD ISSN:0022-152X. CAN 125:300731 AN 1996:582692 CAPLUS. **Abstract**Photocyclization of the substituted 2-(naphth-

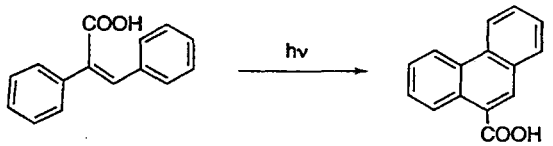
1-yl)-3-(thien-2-yl)propenoic acid in the presence of iodine and air in a benzene-cyclohexane mixt. afforded a separable mixt. of three compds., phenanthro[2,1-*b*]thiophene-10-carboxylic acid, phenanthro[2,1-*b*]thiothene, and naphtho[1,8-*cde*]thieno[3,2-*g*][2]benzopyran.
Thiophene- 19: Citing 5.



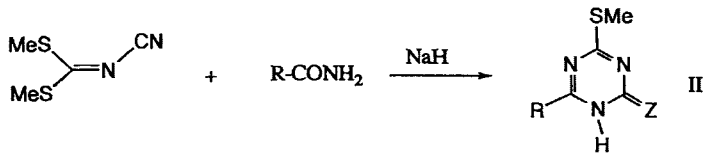

42) **Synthesis of aminopyrimidopyridazines as chemiluminescent compounds by reaction of functionalized maleimide with various amine derivatives.** Tominaga, Yoshinori; Yoshioka, Noriko; Kataoka, Seigo. . *Heterocycles* (1996), **43**(8), 1597-1600. CODEN: HTCYAM ISSN:0385-5414. CAN 125:275783 AN 1996:528752. CAPLUS. **Abstract**-----The reaction of ketene dithioacetal, bis(methylthio)metylene-propanedinitrile, with nitromethane gave 2-hydroxyimino-4-cyano-3-(methylthio)maleimide (I) which was readily converted to the corresponding 4-cyano-3-(methylthio)maleimide (II) by methylation with di-Me sulfate followed by hydrolysis with hydrochloric acid. Compd. II smoothly reacted with various amines, e.g., III, to give the corresponding amino-polycyclic pyrimidines, e.g., IV, contg. a pyrroline ring, which were readily converted to the desired polycyclic pyridazine derivs., e.g., V, in good yields.
KD-104: Fluorescence 4: Citing 18.



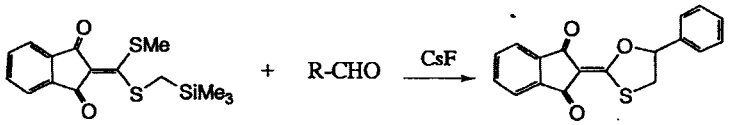

43) **Photocyclization of aryl- and heteroaryl-2-propenoic acid derivatives. Synthesis of polycyclic heterocycles.** Tominaga, Yoshinori; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1996), **33**(3), 523-538. CODEN: JHTCAD ISSN:0022-152X. CAN 125:221450 AN 1996:499131 CAPLUS. **Abstract**----A review with 58 refs. describing the synthetic utility of the photocyclization of aryl- and heteroarylpropenoic acids and their derivs. primarily in the prepn. of heterocyclic compds and the reactions of their photocyclized products.
Citing 12.



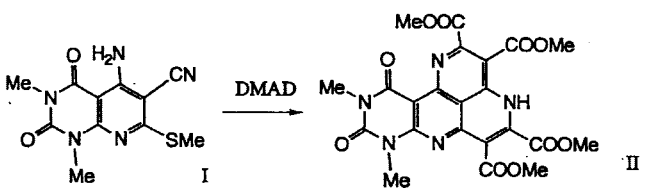

44) **Synthesis of 1,3,5-triazine derivatives by the reaction of S,S'-dimethyl N-cyanocarbonimidodithioate with amides.** Kohra, Shinya; Ueda, Kazuo; Tominaga, Yoshinori. *Heterocycles* (1996), **43**(4), 839-849. CODEN: HTCYAM ISSN:0385-5414. CAN 125:58450 AN 1996:282689 CAPLUS. **Abstract**----- *S,S'*-Dimethyl-*N*-cyanocarbonimidodithioate reacted with amides $RCONH_2$ (R = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, Me) in the presence of sodium hydride in a mixt. of benzene and *N,N*-dimethyl-acetamide to give the corresponding *N*-acyl-*N'*-carbamoyl-S-methylisothioureas $H_2NCON{:}C(SMe)NHCOR$ (I). Refluxing I in methanol gave the corresponding cyclized product, 1,3,5-triazin-2(1*H*)-one derivs. II. II were found to be useful intermediates for the synthesis of trisubstituted 1,3,5-triazines.
KD-103: Citing 4.



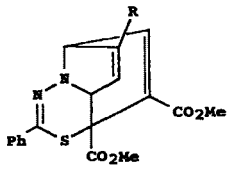
45) **1,3-Dipolar cycloaddition reaction of 2-[(trimethylsilylmethylamino)(methylthio)]methylene-1,3-indandione and 2-[(trimethylsilylmethylthio)(methylthio)]methylene-1,3-indandione: synthetic equivalents of cyclic dicarbonyl alkylideneazomethine and alkylidenethiocarbonyl ylides as novel 1,3-dipolar reagents.** Tominaga, Yoshinori; Takada, Satoshi; Kohra, Shinya. *Chemical & Pharmaceutical Bulletin* (1996), 44(4), 653-60. CODEN: CPBTAL ISSN:0009-2363. CAN 125:10663 AN 1996:243749 CAPLUS. **Abstract**——2-[(Trimethylsilylmethylamino)- (methylamino)- (methylthio)]methylene- and 2-[(trimethylsilylmethylthio)(methylthio)]methylene-1,3-indan- diones (1a, b), which are readily prepd. by reaction of the corresponding 2-bis(methylthio)- methylene- 1,3-indandione with trimethylsilylmethylamine and trimethylsilylmethylmercaptan, were found to be synthetic equivs. of carbonyl alkylidene-azomethine and alkylidene-thiocarbonyl ylides. Reaction of 1a, b with reactive hetero- dipolarophiles such as aldehydes and ketones and reactive alkenes in the presence of cesium fluoride gave 1,3-dipolar cycloadducts, 4,5-dihydro-2-(1,3-dioxoindan-2-ylidene)-1,3-oxazoles, 4,5-dihydro-2-(1,3- dioxoindan-2-ylidene)pyrroles, 2-alkylidene-1,3-oxathiolanes and 2-alkylidenethiophenes, via formation of the counterpart of the carbonyl-substituted with concomitant desilylation.
KD-102: Citing 5.



46) **Synthesis of polycyclic nitrogen-containing heterocycles: one-pot formation of 1,6-naphthyridine ring system by reaction of aminocyanomethylthioheterocycles with dialkyl acetylenedicarboxylates.** Tominaga, Yoshinori; Yoshioka, Noriko. *Heterocycles* (1996), 42(1), 53-6. CODEN: HTCYAM ISSN: 0385-5414.CAN 124:232289 AN 1996:94597 CAPLUS. **Abstract**——The reaction of 5-amino-6-cyano-1,3-dimethyl-7-methylthiopyrido[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (I) with di-Me acetylenedicarboxylate (DMAD) in the presence of potassium carbonate in DMSO gave tetra-Me 8,9,10,11-tetrahydro-8,10-dimethyl-9,10-dioxo-4*H*-pyrimido[4',5':5,6]pyrido[2,3,4-*cb*][1,6]naphthyridine-2,3,5,6-tetracarboxylate (II). The reaction of other heterocycles bearing amino, cyano, and methylthio groups with DMAD or DEAD under the same reaction conditions gave the corresponding tetracyclic heterocycles contg. the fundamental 1,6-naphthyridine ring system.
KD-101: Citing 3.

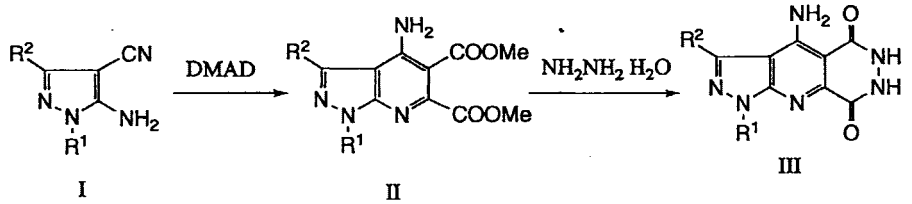


47) **Preparation of new nitrogen-bridged heteorcycles. 41. Reaction of 1-pyridiniothiobenzoylaminides with dimethyl acetylenedicarboxylate.** Kaehi, Akikazu; Ito, Suketqaka; Ishida, Fumihito; Tominaga, Yoshinori. *Heterocycles* (1995), 41(12), 2657-60. CODEN: HTCYAM ISSN:0385-5414. CAN 124:176046 AN 1996:36661 CAPLUS. **Abstract**——The reactions of 1-pyridiniobenzoylaminides with di-Me acetylene-dicarboxylate in chloroform at 50-60°C provided di-Me 5-thia-2,3-diazatricyclo-[4.3.2.02,7]undeca-3,8,10-triene-6,11-dicarboxylate derivs. I (R = H, Me) in moderate yields. The structures of these products were assumed by their spectral and anal. data and detd. finally by the x-ray anal. of one compd.
Citing 2.



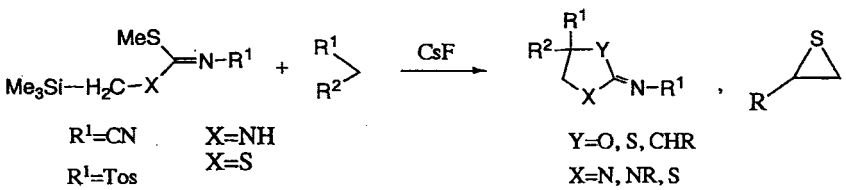
I

48) **Synthesis and chemiluminescence of 1,3-disubstituted pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazine-5,8(6*H*,7*H*)-diones and related compounds.** Tominaga, Yoshinori; Yoshioka, Noriko; Kataoka, Seigo; Aoyama, Norihito; Masunari, Toshiyuki; Miike, Akira. *Tetrahedron Letters* (1995), 36(47), 8641-4. CODEN: TELEAY ISSN:0040-4039. CAN 124:146040 AN 1995:957659 CAPLUS. **Abstract**---- Reactions of 1,3-disubstituted 5-aminopyrazole-4-carbonitrile derivs. I ($R^1$ = Ph, 4-$MeC_6H_4SO_2$, 2-benzothiazolyl, 4-$O_2NC_6H_4$, $R^2$ = H, Me, Ph, 2-thienyl, SMe, etc.) with di-Me acetylenedicarboxylate in the presence of potassium carbonate in DMSO gave the corresponding di-Me 1,3-disubstituted pyrazolo[3,4-*b*]pyridine-5,6-dicarboxylates II which were allowed to react with excess hydrazine hydrate in ethanol under reflux followed by heating at 250-300°C to give the title pyrazolopyridopyridazinediones III in good yields. These tricyclic pyridazine derivs. were evaluated for chemiluminescence. Some were found to be more efficient than luminol in light prodn. III ($R^1$ = Ph, $R^2$ = $SO_2Me$) showed the greatest chemiluminescence intensity derivs. in the presence of $H_2O_2$, peroxidase, in a soln. of phosphate buffer pH 8.0.
KD-100: Fluorescence 3: Citing 19.



I II III

49) ***N*-Bis(methylthio)methylene derivatives. VII. Syntheses and reactions of synthetic equivalents of new 1,3-dipolar reagents using *N*-bis(methylthio)methylene derivatives.** Tominaga, Yoshinori; Ogata, Koichiro; Ueda, Hiroshi; Kohra, Shinya; Hosomi, Akira. *Chemical & Pharmaceutical Bulletin* (1995), 43(9), 1425-34.CODEN: CPBTAL ISSN:0009-2363. CAN 124:117150 AN 1995:902180 CAPLUS. **Abstract**----*N*-Cyano or *N*-(p-toluenesulfonyl)-*N'*-(trimethylsilymethyl)-*S*-methylisothioureas $Me_3SiCH_2NRC(SMe):NR^1$ (R = H, Me, Ph; $R^1$ = cyano, tosyl), readily prepd. by reactions of *S,S'*-dimethyl *N*-cyano- (I) and *S,S'*-dimethyl *N*-(*p*-toluenesulfonyl)- (II) carbonimidodithioates with trimethyl- silyl-methylamine, followed by *N*-alkylation, have been found to provide synthetic equiv. of imino- azomethine ylide. Treatment of these compds. with cesium fluoride in the presence of reactive hetero- dipolarophiles such as carbonyl compds. afforded 1,3-dipolar cycloadducts, 4,5-dihydro-2- iminooxazoles and 4,5-dihydro-2-iminothiazoles, via the 1,3-elimination of (methylthio)trimethylsilane. *S*-Methyl-*S'* trimethylsilylmethyl *N*-cyano- (III) and *N*-(p-toluenesulfonyl)- (IV) carbonimidodithioates, also readily prepd. from the corresponding I and II with (mercaptomethyl)trimethylsilane, were used as new reagents for introducing a thioformaldehyde unit at a carbonyl carbon. Reactions of these compds. with aldehydes in the presence of cesium fluoride afforded thiiranes via the 1,3-dipolar cycloaddn. of iminothiocarbonyl ylide to the C=O double bond. Reactions of III and IV with di-Me fumarate and maleate in the presence of cesium fluoride in acetonitrile gave 1,3-dipolar cycloadducts, di-Me 2-[*N*-(*p*-toluenesulfonyl)imino]tetrahydrothiophene-3,4-dicrboxylates.
KD-99: Citing 8.



$R^1$=CN X=NH
$R^1$=Tos X=S
Y=O, S, CHR
X=N, NR, S

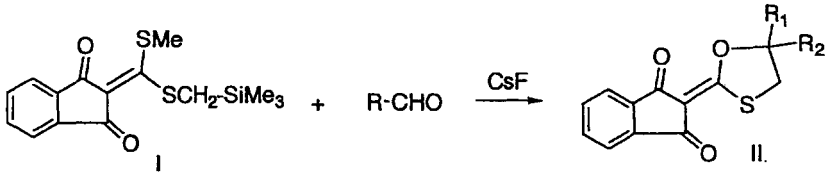
50) **Studies on organosilicon chemistry. 126. Cross-coupling reaction of pentacoordinate alkenylsilicates with organic halides and triflates catalyzed by a palladium complex.** Hojo, Makoto; Murakami,

Chikara; Aihara, Hidenori; Komori, Ei-ichi; Kohra, Shinya; Tominaga, Yoshinori; Hosomi, Akira. *Bulletin de la Societe Chimique de France* (1995), **132**(5-6), 499-508. CODEN: BSCFAS ISSN:0037-8968. CAN 124:55432. AN 1995:819653 CAPLUS. **Abstract**---Isolated pentacoordinate alkoxy-substituted alkenylsilicates, are readily prepd. by mixing alkenyltrialkoxysilane, catechol and triethylamine at room temp. Cross-coupling reactions of these alkenylsilicates with org. halides or triflates are catalyzed by a palladium complex and proceed very smoothly and cleanly to give the corresponding alkenes. The cross-coupling reactions could be also attained by a one pot operation without isolation of pentacoordinate organosilicates. The mechanism of this cross-coupling reaction is also described here. Triethylammonium bis-(catecholato)vinylsilicate (prepn. given), 4-iodonitrobenzene, $PdCl_2(PhCN)_2$ and $P(OEt)_3$ in dioxane were refluxed for 10 h to give 4-nitrostyrene.
Citing 12.

51) **Total $^1H$ and $^{13}C$ chemical shift assignment of indolizino[3,4,5-*ab*]isoindole and 2-methylthiobenz[*f*]imidazo[5,1,2-*cd*]indolizine.** Castle, Lyle W.; Tominaga, Yoshinori; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1995), **32**(3), 1033-8. CODEN: JHTCAD ISSN:0022-152X. CAN 123:143187 AN 1995:658537 CAPLUS.. **Abstract**----The $^1H$ and $^{13}C$ NMR spectral assignment of indolizino[3,4,5-*ab*]isoindole and 2-methylthiobenz[*f*]imidazo[5,1,2-*cd*]indolizine are described. A concerted interpretation of the HMQC, HMQC-TOCSY, HMBC and NOE-difference expts. were used to assign the $^1H$ and $^{13}C$ resonances and indolizino[3,4,5-*ab*]isoindole, whereas for 2-methylthiobenz-[*f*]imidazo[5,1,2-*cd*]indolizine a concerted interpretation of the COSY, HMQC and HMBC expts. were used to generate spectral assignments.
Citing 2.

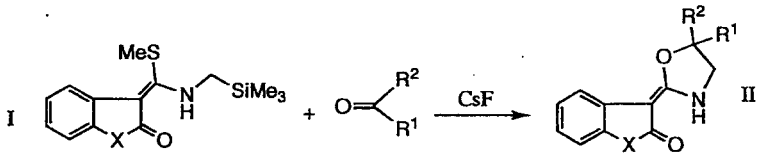
52) **Formal [3 + 2] cycloaddition reactions of 1-methyl-2-[methylthio(trimethylsilylmethylimino)-methylimino]-1,2-dihydropyridine and related compound with carbonyl compounds promoted by fluoride ion.** Kohra, Shinya; Ueda, Kazuo; Tominaga, Yoshinori. *Chemical & Pharmaceutical Bulletin* (1995), **43**(2), 204-9. CODEN: CPBTAL ISSN:0009-2363. CAN 123:111909 AN 1995:440260 CAPLUS. **Abstract**----Reaction of 1-methyl-2-[methylthio(trimethylsilylmethylimino)methylimino]-1,2-dihydropyridine (1), prepd. from 2-amino-1-methylpyridinium iodide in 3 steps, with carbonyl compds. in the presence of 2 equiv of cesium fluoride in acetonitrile afforded 2-(1-methyl-1,2-dihydro-pyridylidene)aminooxazoline derivs., which correspond to formal [3 + 2] cycloadducts of the aminonitrile ylide. Compd. 1 reacted with carbonyl compds. in the presence of a catalytic amt. of $Bu_4BF$ to give corresponding cycloadducts.
KD-98: Citing 9.

53) **1,3-Dipolar cycloaddition reaction of 2-[(trimethylsilylmethylamino)(methylthio)methylene]-1,3-indandione: synthetic equivalent of cyclic dicarbonyl alkylidene-azomethine ylide as a novel 1,3-dipolar reagent.** Tominaga, Yoshinori; Takada, Satoshi; Kohra, Shinya. *Heterocycles* (1995), **40**(1), 105-8. CODEN: HTCYAM ISSN:0385-5414. CAN 122:187466 AN 1995:332246 CAPLUS. **Abstract**----Title indandione I, readily prepd. by reaction of 2-[bis(methylthio)- methylene]-1,3-indandione with trimethylsilylmethylamine, is a synthetic equiv. of carbonyl alkylidene- azomethine ylide. Reaction of I with reactive hetero-dipolarophiles such as aldehydes and ketones and reactive alkenes in the presence of cesium fluoride gave 1,3-dipolar cycloadducts, i.e., oxazolidines II (X = O, $R^1$ = H, $R^2$ = aryl, $R^1 = R^2$ = Ph, etc.) and pyrrolidines II (e.g., X = $CHCO_2Et$, $R^1$ = H, $R_2 = CO_2Et$).
KD-97: Citing 3.

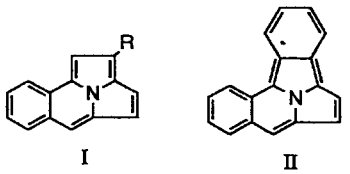



54) **Synthesis and [3+2] cycloaddition reaction of 3-[(trimethylsilylmethylamino)(methylthio)]-methylene-2-coumaranone and -1-methyloxindole: synthetic equivalent of heterocyclic alkylidene-azomethine ylide as a novel 1,3-dipolar reagent.** Tominaga, Yoshinori; Takada, Satoshi; Kohra, Shinya. *Heterocycles* (1994), **39**(1), 15-18. CODEN: HTCYAM ISSN:0385-5414. CAN 122:160526 AN 1995:326724 CAPLUS. **Abstract**----3-[(Trimethylsilylmethylamino)(methylthio)]methylene-2-coumaranone (I, X = O) and -1-methyloxindole (I, X = NMe), readily prepd. by reaction of the corresponding

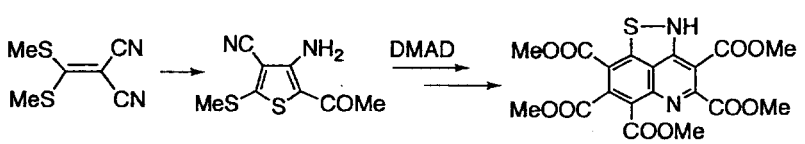
bis(methylthio)methylene-heterocyclic compds. with $H_2NCH_2SiMe_3$, were found to be synthetic equiv. of heterocyclic alkylideneazomethine ylides. Reaction of I with reactive hetero-dipolarophiles such as aldehydes and ketones in the presence of cesium fluoride gave 1,3-dipolar cycloadducts II [same X; $R^1$ = H, Ph; $R^2$ = (un)substituted Ph, 1-naphthyl, $Me(CH_2)_3$, PhCO] via the 1,3-elimination of (methylthio)trimethylsilane.
KD-96: Citing 9.



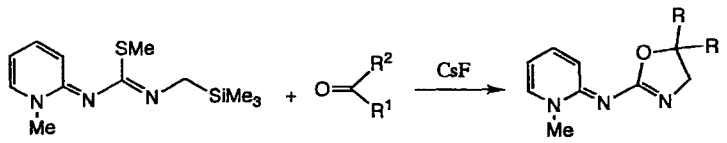

55) **Total assignment of the $^1H$ and $^{13}C$ NMR spectra of pyrrolizino[3,4,5-*ab*]isoquinoline, benzo[1,2]pyrrolizino[3,4,5-*ab*]isoquinoline, and 2-(methylthio)pyrrolizino[3,4,5-ab]isoquinoline.** Castle, Lyle W.; Tominaga, Yoshinori; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1994), **31**(5), 1209-17. CODEN: JHTCAD ISSN:0022-152X. CAN 121:300384 AN 1994:700384 CAPLUS. **Abstract**-----The 1H and 13C NMR spectra of the title compds. I (R = H, SMe) and II are assigned using COSY, HMQC, HMBC and NOE-difference expts.
Citing 2.



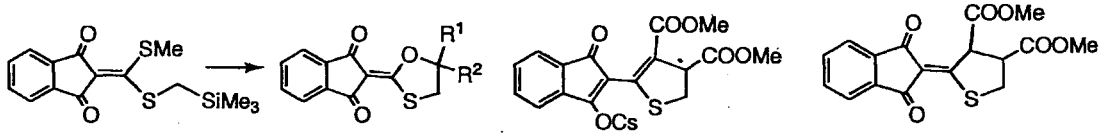

56) **The reaction of methyl 3-amino-4-cyano-5-methylthiothiophene-2-carboxylate with DMAD. A new synthesis of polyfunctionalized quinolines.** Tominaga, Yoshinori; Luo, Jiann-Kuan; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1994), **31**(4), 771-3. CODEN: JHTCAD ISSN:0022-152X. CAN 121:255767 AN 1994:655767 CAPLUS. **Abstract**------The reaction of Me 3-amino-4-cyano-5-(methylthio)-2-thiophenecarboxylate (I), which was prepd. by the reaction of [bis(methylthio)-methylene]propanedinitrile with Me thioglycolate followed by di-Me acetylenedicarboxylate (DMAD) in the presence of potassium carbonate in DMSO gave the polyfunctionalized quinoline, pentamethyl 4-amino-5-mercaptoquinoline-2,3,6,7,8-pentacarboxylate. The oxidn. of the latter with iodine in DMSO provided the novel ring system in the form of the deriv., pentamethyl 2*H*-isothiazolo[3,4,5-*de*]quinoline-3,4,6,7,8-pentacarboxylate (II).
KD-95: Citing 11.



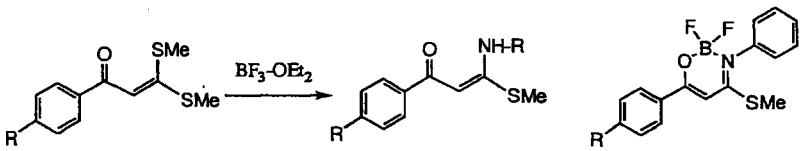

57) **Fluoride ion promoted azomethine ylide generation from 1-methyl-2-[methylthio(trimethylsilyl-methylimino)methylimino]-1,2-dihydropyridine, a synthetic equivalent of aminonitrile ylide.** Kohra, Shinya; Tominaga, Yoshinori. *Heterocycles* (1994), **38**(6), 1217-20. CODEN: HTCYAM ISSN:0385-5414. CAN 121:134011 AN 1994:534011 CAPLUS. **Abstract**-----1-Methyl-2-[methylthio(trimethyl-silylmethylimino)methylimino]-1,2-dihydropyridine, prepd. from 2-amino-1-methyl- pyridinium iodide in 3 steps, reacted with carbonyl compds. in the presence of cesium fluoride in acetonitrile to give 2-(1-methyl-1,2-dihydropyridylidene)aminooxazoline derivs. I (R = aryl) via the 1,3-dipolar cycloaddn. This reaction was the first example of reaction aminonitrile ylide with the C:O double bond.
KD-94: Citing 6.



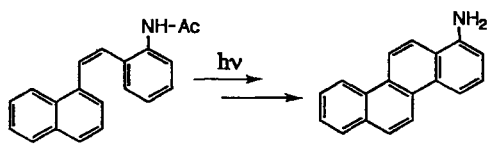
58) ***S*-Silylmethyl-substituted ketene dithioacetals as synthetic equivalent of a novel 1,3-dipolar reagent, alkylidenethiocarbonyl ylide; synthesis and [3+2] cycloaddition reactions.** Tominaga, Yoshinori; Takada, Satoshi; Kohra, Shinya. *Tetrahedron Letters* (1994),35(21), 3555-8. CODEN: TELEAY ISSN:0040-4039. CAN 121:108587 AN 1994:508587 CAPLUS. **Abstract**----2-[(Trimethylsilyl- methylthio)(methylthio)-methylene]-1,3-indanedione (I; R = $SiMe_3$), readily prepd. by reaction of 2-bis- (methylthio)methylene-1,3-indanedione(I; R = H) with (trimethysilyl)methylmercaptan, $Me_3SiCH_2SH$, was shown to be the synthetic equiv. of alkylidene-thiocarbonyl ylide. Treatment of this compd. with fluoride ions in the presence of reactive hetero-dipolarophiles such as carbonyl compds. and active alkenes afforded 1,3-dipolar cycloadducts, e.g. II, 2-alkyliden-1,3-oxathiolanes III ($R^1$ = Ph, 4-$MeC_6H_4$, 3-, 4-$MeOC_6H_4$, 4-$ClC_6H_4$, 2,6-$Cl_2C_6H_3$, 4-$PhC_6H_4$, 4-$NCC_6H_4$, 2-$O_2NC_6H_4$, 1-naphthyl, PhCH:CH, $R^2$ = H; $R^1$ = $R^2$ = $CO_2Et$; $R^1$ = 4-$O_2NC_6H_4$, $R^2$ = Me) and 2-alkylidenethiophenes IV ($R^3$ = $CO_2Me$, H), by carbonyl-substituted counterparts and concomitant desilylation.
KD-93: Citing 7.



59) **Reaction of a-oxoketene dithioacetals with arylamines in the presence of boron trifluoride etherate for the synthesis of ketene *S,N*-acetals.** Kohra, Shinya; Turuya, Shinichiro; Kimura, Munefumi; Ogata, Koichiro; Tominaga,Yoshinori. *Chemical & Pharmaceutical Bulletin* (1993), **41**(7), 1293-6. CODEN: CPBTAL ISSN:0009-2363. CAN 120:298175 AN 1994:298175 CAPLUS. **Abstract**------ Reaction of α-oxoketene dithioacetals I (R = H, Me, MeO, Br, Cl) or the corresponding 2-furyl or 2-thienyl acetals with $R^1NH_2$ ($R^1$ = Ph, 2-, 4-$ClC_6H_4$, 2-, 4-$BrC_6H_4$, 4-$MeC_6H_4$, 2,3-$Cl_2C_6H_3$) was accelerated by catalytic $BF_3$-$OEt_2$ to give 62-98% *S,N*-acetals II selectively. Using stoichiometric $BF_3$-$OEt_2$ gave 82-99% borate complexes III.
KD-92: Citing 5.

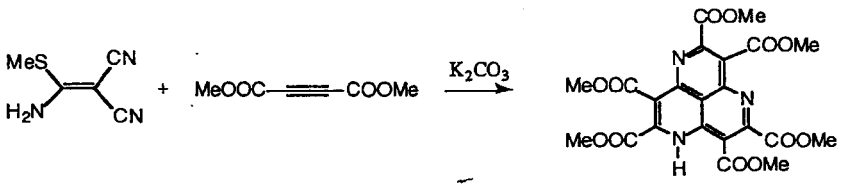


60) **Synthesis of aminochrysenes by the oxidative photocyclization of acetylaminostilbenes.** Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. *Chemical & Pharmaceutical Bulletin* (1993), **41**(10), 1853-5. CODEN: CPBTAL ISSN:0009-2363. CAN 120:269809 AN 1994:269809 CAPLUS. **Abstract**---Aminochrysene derivs. were synthesized by the oxidative photocyclization of acetylamino-stilbenes in the presence of iodine and air, followed by hydrolysis. Thus, acetylaminostyrylnaphthalene I, prepd. via Wadsworth-Emmons reaction of di-Et 1-naphthylmethylphosphonate and 2-$O_2NC_6H_4CHO$, underwent oxidative photocyclization to give 67% 1-(acetylamino)chrysene (II, R = Ac), which was hydrolyzed in HCl-EtOH to give 83% II (R = H).
Citing 4.



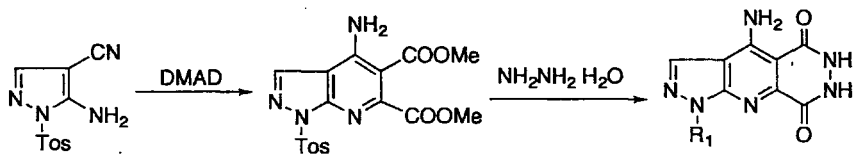
61) **Synthesis of the novel tricyclic heterocycle, 1*H*-1,4,7-triazaphenalene, pyridine-containing ring system: hexamethyl 1*H*-1,4,7-triazaphenylene-2,3,5,6,8,9-hexacarboxylate.** Tominaga, Yoshinori; Nomoto,

Kenichi. *Heterocycles* (1994), 37(1), 235-8. CODEN: HTCYAM ISSN:0385-5414. CAN 120:245009 AN 1994:245009 CAPLUS. **Abstract**---The reaction. of 3-amino-3-methylthio-2-cyanoarylonitrile (I) with excess di-Me acetylenedicarboxylate(DMAD) in the presence of K carbonate in DMSO gave a novel tricyclic heterocycle, hexamethyl 1*H*-1,4,7-triazaphenalene-2,3,5,6,8,9-hexacarboxylate (II). When one equiv. of DMAD was used in this reaction., di-Me 4-amino-3-cyano-2-methylthiopyridine-5,6-dicarboxylate, a key intermediate of II was obtained.
KD-91: Citing 5.

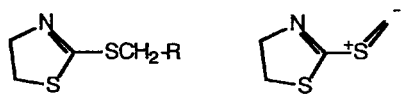


62) **Synthesis of heterocyclic compounds using ketene dithiocetals.** Tominaga, Yoshinori. *Trends in Heterocyclic Chemistry* (1991), 2 43-83. CODEN: TIHCE6 CAN 120:244724 AN 1994:244724 CAPLUS. **Abstract**-----A review with 191 refs. Major emphasis is placed on the results obtained in the authors' own lab., along with addnl. important results reported by other groups.
KD-90: Citing 33.

63) **Polycyclic pyridazines. II. Synthesis of pyrazolo[4',3':5,6]pyrido[2,3-d]pyridazine derivatives from dimethyl pyrazolo[3,4-*b*]pyridazine-5,6-dicarboxylates as the key intermediates.** Tominaga, Yoshinori; Luo, Jiann Kuan; Castle, Lyle W.; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1993), 30(1), 267-73. CODEN: JHTCAD ISSN:0022-152X. CAN 120:217563 AN 1994:217563 CAPLUS. **Abstract**----The prepn. of the novel pyrazolo[4',3':5,6]pyrido[2,3-d]pyridazine ring system, for example I and some of its derivs. was accomplished. Also, 4-amino-1-phenyl-5,8-dioxo-, 4-amino-5,8-dioxo-, 1-phenyl-5,8-dioxo-, 5,8-dioxo-, 5,8-dichloro-1-phenyl-, 5-ethoxy-1-phenyl- and 8-ethoxy-1-phenyl-pyrazolo[4',3':5,6]pyrido[2,3-*d*]pyridazines were prepd.
KD-89: Fluorescence 2: Citing 13.



64) **Preparation of new thiocarbanion species bearing thiazolinyl and benzothiazolyl groups and reactions with carbonyl compounds.** Kohra, Shinya; Ueda, Hiroshi; Tominaga, Yoshinori. *Heterocycles* (1993), 36(12), 2673-6. CODEN: HTCYAM ISSN:0385-5414. CAN 120:217395 AN 1994:217395 CAPLUS. **Abstract**-----2-[(Trimethylsilyl)methylthio]thiazoline (I; R = $SiMe_3$) reacted with arom. aldehydes in the presence of cesium fluoride or tris(dimethylamino)sulfur(trimethylsilyl)difluoride (TASF) to give 2-heteroarylthioethanol or thiirane derivs. in good yields. The reactions of 2-[(trimethylsilyl)-methylthio]benzothiazole with arom. aldehydes are also discussed. E.g., reaction of I (R = $SiMe_3$) with benzaldehyde in THF contg. TASF gave 90% I [R = CH(OH)Ph].
Citing 3.



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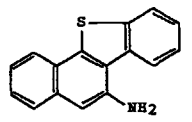
65) **Synthesis of 6-aminobenzo[*b*]naphtho[2,1-*d*]thiophene.** Tominaga, Yoshinori; Castle, Lyle W.; Castle, Raymond N. *Journal of Heterocyclic Chemistry* (1993), 30(3), 845-7. CODEN: JHTCAD ISSN:0022-152X. CAN 120:191452 AN 1994:191452 CAPLUS. **Abstract**------The title compd., (I) was prepd. in a one-pot synthesis. I has a structural resemblance to 5-aminochrysene which is related to known carcinogens.
Thiophene-19: Citing 1.



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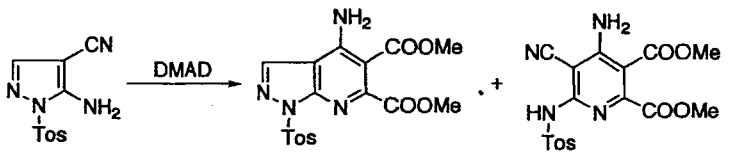
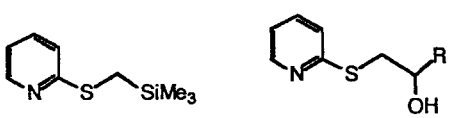
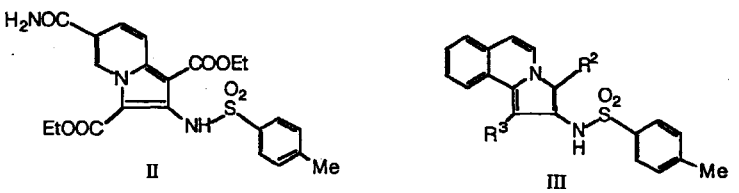
66) **Diels-Alder reaction of 5-aminopyrazole-4-carbonitrile with DMAD: synthesis and structural determination of dimethyl 2-(*p*-toluenesulfonylamino)-3-cyano-4-imino-1,4-dihydropyridine-5,6-dicarboxylate.** Tominaga, Yoshinori; Castle, Raymond N.; Dalley, N. Kent. *Journal of Heterocyclic Chemistry* (1993), **30**(1), 295-9. CODEN: JHTCAD ISSN:0022-152X. CAN 120:8452 AN 1994:8452 CAPLUS. **Abstract**——The Diels-Alder reaction of 5-amino-1-(*p*-toluenesulfonyl)-pyrazole-4-carbonitrile with di-Me acetylenedicarboxylate (DMAD) was carried out in the presence of $K_2CO_3$ in DMSO. The reaction gave di-Me 2-(*p*-toluenesulfonylamino)-3-cyano-4-imino-1,4- dihydro- pyridine-5,6-dicarboxylate (shown as tautomeric amino deriv. I). The product was formed by transformation of the original Diels-Alder adduct II followed by rearrangement of the p-toluenesulfonylamino group into the 2-position of the pyridine ring. The structure of the product was established by x-ray crystallog. This reaction is the first example of a pyrazole ring serving as the diene in a [4 + 2] cycloaddn. reaction.
Fluorescence-1: Citing 4.



67) **Reaction of 2-trimethylsilylmethylthiopyridine promoted by a fluoride ion: the first example of generation of 2-pyridylthiomethyl carbanion.** Kohra, Shinya; Ueda, Hiroshi; Tominaga, Yoshinori. *Heterocycles* (1993), **36**(7), 1497-500. CODEN: HTCYAM ISSN:0385-5414. CAN 120:8443 AN 1994:8443 CAPLUS. **Abstract**——2-Trimethylsilylmethylthiopyridine prepd. readily by the reaction of 2-mercaptopyridine with chloromethyltrimethylsilane in the presence of potassium carbonate reacts with carbonyl compds. in the presence of a catalytic amt. of tetrabutylammonium fluoride to give 2-(2-pyridylthio)ethanols and with alkenes to give 2-pyridylthioalkanes. This reaction is the first example of generation and introduction of 2-pyridylthiomethyl carbanion.
Citing 2.



68) ***N*-Bis(methylthio)methylene derivatives. 5. New synthesis of 2-aminoindolizine and related compounds via a formal [3 + 3] cycloaddition reaction using *N*-bis(ethoxycarbonylmethylthio)-methylenephenylsulfonamides.** Tominaga, Yoshinori; Ueda, Hiroshi; Ogata, Koichiro; Kohra, Shinya. *Journal of Heterocyclic Chemistry* (1992), **29**(1), 209-14. CODEN: JHTCAD ISSN:0022-152X. CAN 117:111422 AN 1992:511422 CAPLUS. **Abstract**——Reaction of *N*-ethoxycarbonylmethylene-pyridine with $4\text{-}RC_6H_4SO_2N{:}C(SR^1)_2$ (I, R = Me, NHAc; $R^1 = CH_2CO_2Et$) in the presence of $Et_3N$ as a base in EtOH gave indolizinedicarboxylates II via a new formal [3 + 3] cycloaddn. reaction. In a similar manner, 2-sulfonylaminopyrrolo[2,1-*a*]isoquinolines III ($R^2 = CO_2Et$, $CO_2Me$; $R^3 = CO_2Et$, cyano) were obtained by the reaction of I and $4\text{-}MeC_6H_4SO_2N{:}C(SMe)SR^3$ with the isoquinoline *N*-ylides IV with good results.
KD-88: Citing 4.

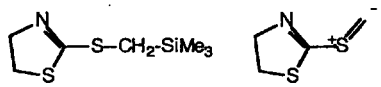


II III

69) **Synthesis of organosilicon compounds as synthetic equivalents of unstable active chemical species and**

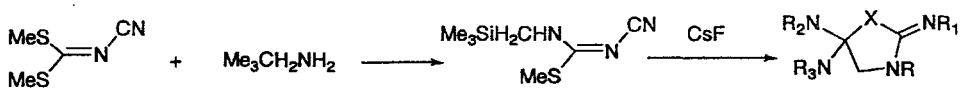
**their applications to highly selective synthesis of heterocycles.** Tominaga, Yoshinori; Hojo, Makoto; Hosomi, Akira. *Yuki Gosei Kagaku Kyokaishi* (1992), **50**(1), 48-60. CODEN: YGKKAE ISSN:0037-9980. CAN 116:174188 AN 1992:174188 CAPLUS. **Abstract**-----A review with 27 refs. on the synthesis of Si analogs of azomethine ylides, iminoazomethine ylides, thiocarbonyl ylides, and iminothiocarbonyl ylides. Cycloaddn. reactions of the Si compds. with a variety of dipolarophiles and hetero-dipolarophiles for regio- and stereoselective prepn. of heterocyclic compds. are also discussed.
Citing 14.

70) **Studies on organosilicon chemistry. 111. New synthesis of thiiranes by fluoride ion-promoted reaction of *S*-methyl-*S'*-trimethylsilylmethyl *N*-(*p*-toluenesulfonyl)dithioiminocarbonate and 2-(trimethylsilylmethylthio)thiazoline with aldehydes. *S*-methyl-*S"*-trimethylsilylmethyl *N*-(*p*-toluene-sulfonyl)dithioiminocarbonate and 2-(trimethylsilylmethylthio)thiazoline with aldehdyes.** Tominaga, Yoshinori; Ueda, Hiroshi; Ogata, Koichiro; Kohra, Shinya; Hojo, Makoto; Ohkuma, Masakazu; Tomita, Kyoji; Hosomi, Akira. *Tetrahedron Letters* (1992), **33**(1), 85-8. CODEN: TELEAY ISSN:0040-4039. CAN 116:151454 AN 1992:151454 CAPLUS. **Abstract**-----The title dithioiminocarbonates I and $Me_3SiCH_2SC(SMe)$:NTs, readily prepd. by the reaction of $(MeS)_2C$:NTs and 2-mercaptothiazoline with (chloromethyl)trimethylsilane in the presence of a base, were used as new reagents for the introduction of a thioformaldehyde unit to a carbonyl carbon. The reaction of these compds. with aldehydes in the presence of CsF afforded thiiranes via the 1,3-dipolar cycloaddn. of iminothiocarbonyl ylide to C:O double bond.
Citing 10.

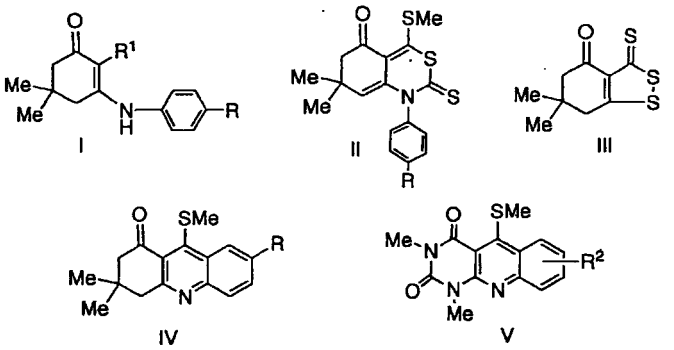


I

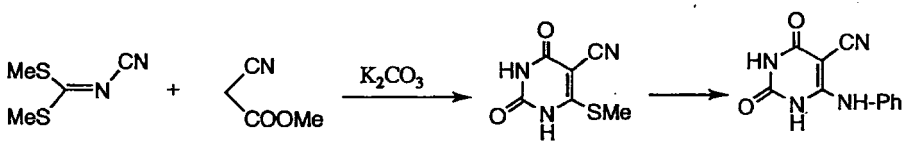
71) **Studies on organosilicon chemistry. 111. Synthesis and [3+2]cycloadditions of *N*-(trimethyl-silylmethyl)isothioureas: a synthetic equivalent of novel 1,3-dipolar reagent, iminoazomethine ylid.** Tominaga, Yoshinori; Ogata, Koichiro; Kohra, Shinya; Hojo, Makoto; Hosomi, Akira. *Tetrahedron Letters* (1991), **32**(42), 5987-90. CODEN: TELEAY ISSN:0040-4039. CAN 116:6458 AN 1992:6458 CAPLUS. **Abstract**-----*N*-(Trimethylsilylmethyl)isothioureas $Me_3SiCH_2NRC(SMe)$:$NR^1$ (I; R = H, Me, $R^1$ = $SO_2C_6H_4Me$-4; R = H, Me, $CH_2Ph$, $R^1$ = CN) readily prepd. by the reaction of $(MeS)_2C$:$NR^1$ with $Me_3SiCH_2NH_2$ followed by *N*-alkylation, are iminoazomethine ylide synthetic equiv. Treatment of I with CsF in the presence of reactive heterodipolarophiles such as carbonyl compds. afforded 1,3-dipolar cycloadducts, 2-iminooxazolidines and 2-iminothiazolidines II [X = O, $R^2$ = H, $R^3$ = Ph, substituted Ph, 1-naphthyl, (E)-PhCH:CH, Bu; X = O, $R^2$ = Ph, $R^3$ = Ph, PhCO; X = S, $R^2$ = 4-$MeOC_6H_4$, $R^3$ = 2-benzo[*b*]-thienyl] via 1,3-elimination of (methylthio)trimethylsilane.
KD-87: Citing 10.



72) **Reaction of enaminones with carbon disulfide: synthesis of heterocycles using enamino dithiocarboxylates.** Tominaga, Yoshinori; Okuda, Hiroto; Kohra, Shinya; Mazume, Hisako. *Journal of Heterocyclic Chemistry* (1991), (5), 1245-55. CODEN: JHTCAD ISSN:0022-152X. CAN 115:279849 AN 1991:679849 CAPLUS. **Abstract**-----Reaction of various types of enaminones, e.g, I (R = H, Cl, Me, OMe; $R^1$ = H) with carbon disulfide in the presence of sodium hydroxide as the base in DMSO to give the corresponding enamino dithiocarboxylates I ($R^1$ = $CS_2Me$), 1,3-thiazines, e.g., II, and trithiones, e.g., III. Enamino dithiocarboxylates are cyclized under refluxing in di-Ph ether to give the acridine derivs. IV ($R^1$ = H, Me). The reaction of 6-arylamino-1,3-dimethyluracils with excess carbon disulfide in the presence of sodium hydroxide and subsequent methylation with di-Me sulfate gave directly the corresponding thiopyrimidoquinolinediones V ($R^2$ = H, 7-Me, 7-, 8-, or 9-OMe).
CS-48: Citing 9.



73) **Synthesis of pyrimidine derivatives using *N*-bis(methylthio)methylenecyanamide.** Tominaga, Yoshinori; Ohno, Syuichirou; Kohra, Shinya; Fujito, Hiroshi; Mazume, Hisako. *Journal of Heterocyclic Chemistry* (1991), **28**(4), 1039-42. CODEN: JHTCAD IS SN:0022-152X. CAN 115:183231 AN 1991:583231 CAPLUS. **Abstract**-----$(MeS)_2C{:}NCN$ reacted with active methylene compds. (Me cyanoacetate, di-Me malonate, Et acetoacetate, Et phenylacetate) in the presence of $K_2CO_3$ or KOH in DMSO followed by the treatment using an appropriate base or acid to give the corresponding 6-methylthiouracil derivs. I (R = SMe, $R^1$= cyano, $CO_2Me$, COMe, Ph) in 15-80% yields. These uracil derivs. are useful intermediates for the synthesis of 6-aminouracils and fused pyrimidine derivs. Thus, the reactions of I (R = SMe, $R^1$ = cyano) with $H_2NXH$ (X = O, NH, NPh) gave isoxazolopyrimidine II (X = O) and pyrazolopyrimidines II (X = NH, NPh) resp. $R^2NH_2$ ($R^2$ = Ph, substituted Ph, $PhCH_2$) reacted with I (R = SMe, $R^1$ = cyano) to give I ($R = NHR_2$).
KD-86: Citing 9.

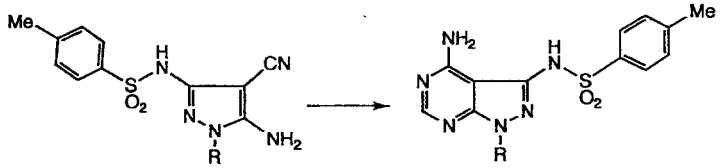


74) **New synthesis and Diels-Alder reactions of 2-aminomethyl-1,3-butadienes and related 1,3-dienes.** Hosomi, Akira; Masunari, Toshiyuki; Tominaga, Yoshinori; Hojo, Makoto. *Bulletin of the Chemical Society of Japan* (1991), **64**(3), 1051-3. CODEN: BCSJA8 ISSN:0009-2673. CAN 114:228318 AN 1991:228318 CAPLUS. **Abstract**----The Diels-Alder reaction of 2-[(dialkylamino)methyl]-1,3-butadienes with various dienophiles gave 1-[(dialkylamino)methyl]-1-cyclohexenes. Thus, reaction of $CH_2{:}C(CH_2NMe_2)CH{:}CH_2$ with Me acrylate gave a 38:62 mixt. of regioisomeric Me 3- and 4-[(dimethylamino)methyl]-3-cyclohexene-1-carboxylate. The substitution reaction of the latter with $NaCH(CO_2Et)_2$ gave Me 3- and 4-[2,2-bis(ethoxycarbonyl)ethyl]-3-cyclohexene-1-carboxylate. The Diels-Alder reaction of $CH_2{:}C(CH_2NMe_2)CH{:}CH_2$ di-Me fumarate was stereospecific.
Citing 4.

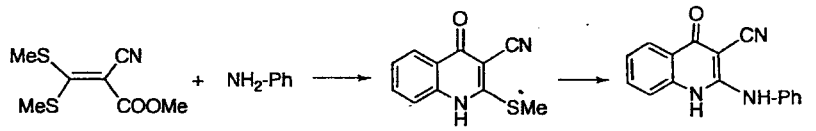
75) **Organosilicon chemistry. 107. 2-Trimethylsilylethyl-1,3-butadiene as a synthetic equivalent of parent cross-conjugated hexatriene, 3-methylene-1,4-pentadiene.** Hosomi, Akira; Masunari, Toshiyuki; Tominaga, Yoshinori; Yanagi, Toshiharu; Hojo, Makoto. *Tetrahedron Letters* (1990), **31**(43), 6201-4. CODEN: TELEAY ISSN:0040-4039. CAN 114:102165 AN 1991:102165 CAPLUS. **Abstract**----2-Trimethylsilylethyl-1,3-butadiene, readily prepd. by the cross-coupling reaction of the Grignard reagent of 3-bromo-3-butenyltrimethylsilane with vinyl bromide catalyzed by a nickel-phosphine complex, works as a synthetic equiv. to 3-methylene-1,4-pentadiene [parent [3] dendralene] by the consecutive Diels-Alder reactions.
Citing 8.

76) **Synthesis of 3-aminopyrazolo[3,4-*d*]pyrimidine derivatives using *N*-bis(methylthio)methylene-*p*-toluenesulfonamide.** Tominaga, Yoshinori; Hara, Mayumi; Honkawa, Harumasa; Hosomi, Akira. *Journal of Heterocyclic Chemistry* (1990), **27**(5), 1245-8. CODEN: JHTCAD ISSN:0022-152X. CAN 114:23915 AN 1991:23915 CAPLUS. **Abstract**-----p-$MeC_6H_4SO_2N{:}C(SMe)_2$ reacted with active- methylene compds. such as $NCCH_2R$ (R - cyano, $CONH_2$) to give the corresponding p-$MeC_6H_4SO_2NHC(SMe){:}CRCN$ (I), which were convenient starting materials for the synthesis of 3,5-diaminopyrazole derivs. II. Cyclocondensation

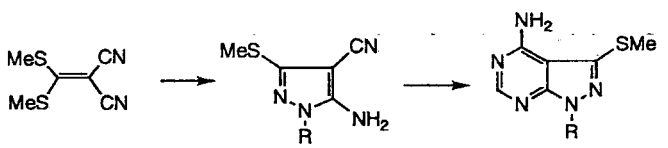
reaction of I with hydrazines gave the corresponding II, key intermediates for the synthesis of 3-aminopyrazolo[4,5-*d*]pyrimidine derivs. III ($R^1$ = H, Ph, p-$O_2NC_6H_4$; $R^2$ = $NH_2$, OH).
KD-85: Citing 6.



77) **Synthesis of quinoline derivatives using ketene dithioacetals.** Tominaga, Yoshinori; Michioka, Takeharu; Moriyama, Kohu; Hosomi, Akira. *Journal of Heterocyclic Chemistry* (1990), 27(5), 1217-25. CODEN: JHTCAD ISSN:0022-152X. CAN 114:23780 AN 1991:23780 CAPLUS. **Abstract**——$RC_6H_4NHC(SMe):C(CN)CO_2Me$ (R = H, 4-Me, 2-MeO, 3-MeO, 4-MeO, 2-Cl, 4-Cl, 4-Br), which are readily prepd. by the reaction of $(MeS)_2C:C(CN)CO_2Me$ (I) with $RC_6H_4NH_2$, was heated at reflux in Ph2O to give the corresponding methylthiohydroxyquinolinecarbonitriles II in 14-77% yields. The reaction of I with excess $RC_6H_4NH_2$ in $Ph_2O$ at reflux gave the 2-(arylamino)-4-hydroxy- quinolinecarbonitriles III.
KD-84: Citing 17.

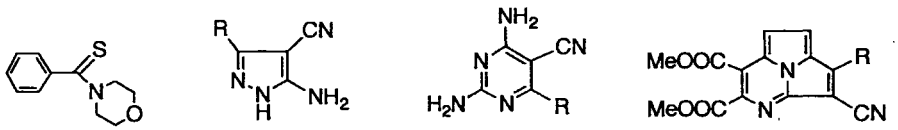


78) **Synthesis of pyrazolo[3,4-*d*]pyrimidine derivatives using ketene dithioacetals.** Tominaga, Yoshinori; Honkawa, Yasumasa; Hara, Mayumi; Hosomi, Akira. *Journal of Heterocyclic Chemistry* (1990), 27(3), 775-83. CODEN: JHTCAD ISSN:0022-152X. CAN 113:211929 AN 1990:611929 CAPLUS. **Abstract**——The cyclization of 5-amino-3-methylthiopyrazole-4-carbonitriles or 4-carboxamides, which were prepd. by the reaction of ketene dithioacetals [bis(methylthio)methylenemalononitrile, bis(methylthio)methylene-cyanoacetamide] with hydrazines (hydrazine hydrate, phenylhydrazine, *p*-chlorophenylhydrazine, *p*-nitrophenylhydrazine), with formamide or carbon disulfide proceeded to give the corresponding 4-amino- or 4-hydroxy-3-methylthiopyrazolo[3,4-*d*]pyrimidines in good yields. 3-Aminopyrazolo[3,4-*d*]pyrimidine derivs. were also obtained by the application of the cyclization reaction of 3,5-diaminopyrazoles with formamide. E.g., pyrazolopyrimidine I was obtained in 72% yield from aminopyrazolecarbonitrile II with $HCONH_2$.
KD-83: Citing 62.



79) **Polarized ethylenes. IV. Synthesis of polarized ethylene using thioamides and methyl dithiocarboxylates and their application to syntheses of pyrazoles, pyrimidines, pyrazolo-[3,4-*d*]pyrimidines and 5-aza[2.2.3]cyclazines.** Tominaga, Yoshinori; Matsuoka, Yoshiki; Oniyama, Yukio; Uchimura, Yoshimitsu; Komiya, Hirofumi; Hirayama, Michiyo; Kohra, Shinya; Hosomi, Akira. *Journal of Heterocyclic Chemistry* (1990), 27(3), 647-60. CODEN: JHTCAD ISSN:0022-152X. CAN 113:171975 AN 1990:571975 CAPLUS. **Abstract**——Polarized ethylenes, e.g., $RR^1C:C(CN)_2$ (R = Ph, substituted Ph, 2-thienyl, CH2Ph, SMe; $R^1$ = SMe, morpholino), having both electron-donating (an amino or a methylthio group) and electron-accepting (cyano, carbamoyl, Me ester) groups on the adjacent 2 olefinic carbon atoms were prepd. by the condensation of S-alkylthioamidinium salts or Me phenyldithiocarboxylates with the corresponding active methylene compds. in good yields. These polarized ethylenes were alternatively synthesized by the reaction of thioamides or Me dithiocarboxylates with tetracyanoethylene oxide in good yields. Reactions of these polarized ethylenes with hydrazine or guanidine derivs. occurred smoothly to give pyrazoles I (R = Ph, $CH_2Ph$, substituted Ph, 2-thienyl) and pyrimidines II (R = Ph, $CH_2Ph$, substituted Ph) in good yields. The synthesis of 5-aza[2.2.3]cyclazine deriv., III ($R^1$ = morpholino, pyrrolidino, piperidino) using polarized ethylenes is also described.

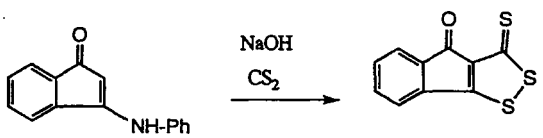
Citing 41.



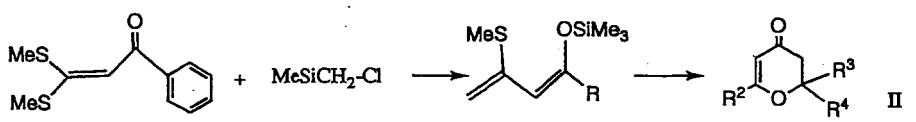
80) **Studies of organosilicon chemistry. 107. *N*-(silylmethyl)-substituted ketene *N,S*-acetals as a synthetic equivalent of a novel 1,3-dipolar reagent, alkylideneazomethine ylides: synthesis and [3 + 2] cycloadditions.** Hosomi, Akira; Miyashiro, Yuji; Yoshida, Ryoji; Tominaga, Yoshinori; Yanagi, Toshiharu; Hojo, Makoto. *Journal of Organic Chemistry* (1990), 55(19), 5308-10. CODEN: JOCEAH ISSN:0022-3263. CAN 113:171954 AN 1990:571954 CAPLUS. **Abstract**-----A variety of *N*-silylmethyl-substituted ketene *N,S*-acetals, readily prepd. by the reaction of ketene dithioacetals with trimethylsilylmethylamine in MeOH at reflux followed by *N*-alkylation, were allowed to react smoothly with activated alkenes, carbonyl compds., and thioketones, to afford the corresponding α-alkylidenepyrrolidines, oxazolidines, and thiazolidines, resp., via a 1,3-elimination of methylthiotrimethylsilane. These reagents can be viewed as a storable and easy to handle synthetic equiv. of alkylideneazomethine ylid.
KD-82: Citing 14.

81) **Polarized ethylene. V. Synthesis of 1-substituted indolizine, pyrazolo[1,5-*a*]pyridine, and their related compounds using methoxyethylene derivatives.** Tominaga, Yoshinori; Ichihara, Yuichi; Mori, Tomoko; Kamio, Chizuko; Hosomi, Akira. *Journal of Heterocyclic Chemistry* (1990), 27(2), 263-8. CODEN: JHTCAD ISSN:0022-152X. CAN 113:59011 AN 1990:459011 CAPLUS. **Abstract**-----Reaction of pyridiniums I (R = $CO_2Et$, CN) with $MeOCH{:}CHR^1$ ($R^1$ = COMe, COPh, $COC_6H_4Br$-4, CN, $CO_2Me$) gave indolizines II in 22-56% yield. Similar reaction of isoquinoliniums, aminopyridiniums, and -quinoliniums gave pyrrolo[2,1-*a*]isoquinolines, pyrazolo[1,5-*a*]pyridines, and pyrazolo[1,5-*a*]quinolines, resp.
KD-81: Citing 17.

82) **A new route to 1,2-dithiole-3-thiones (trithiones) by the reaction of enaminones with carbon disulfide.** Tominaga, Yoshinori; Norisue, Hajime; Kamio, Chizuko; Masunari, Toshiyuki; Miyashiro, Yuji; Hosomi, Akira. *Heterocycles* (1990), 31(1), 1-4. CODEN: HTCYAM ISSN:0385-5414. CAN 113:40514 AN 1990:440514 CAPLUS. **Abstract**-----Enaminones reacted with carbon disulfide in the presence of sodium hydroxide to give the corresponding 1,2-dithiol-3-thiones(trithiones) in 30-82% yields. E.g., oxoindenodithiolethione I was obtained in 78% yield from enaminone II.
CS-48: Citing 3.



83) **Studies on organosilicon chemistry. 105. α-Oxo ketene dithioacetals in organic synthesis. A new access to 1-siloxy-1,3-butadienes and their selective reactions with electrophiles.** Tominaga, Yoshinori; Kamio, Chizuko; Hosomi, Akira. *Chemistry Letters* (1989), (10), 1761-4. CODEN: CMLTAG ISSN:0366-7022. CAN 112:197746 AN 1990:197746 CAPLUS. **Abstract**-----Reactions of -oxo ketene dithioacetals $R1COCR^2{:}C(SMe)_2$ [$R^1$ = Ph, $4\text{-}ClC_6H_4$, $4\text{-}MeOC_6H_4$, $Me_3C$, 2-furyl, 2-thienyl, $R^2$ = H; R1R2 = (CH2)4] with $Me_3SiCH2MgCl$ in the presence of CuI gave $Me3SiOCR1{:}CR^2C(SMe){:}CH_2$ (I) selectively in excellent yields. I reacted with various carbon electrophiles such as carbonyl compds. to furnish the dienones $R^1COCH{:}C(SMe)CH{:}CR^3H$ ($R^1$ = Ph, $4\text{-}ClC_6H_4$, $4\text{-}MeOC_6H_4$, 2-thienyl; $R^3$ = Ph, $4\text{-}ClC_6H_4$) and pyrones, e.g., II [$R^1$ = Ph, $4\text{-}ClC_6H_4$; $R^3$ = Ph, $4\text{-}ClC_6H_4$, $R^4$ = H, Me; $R^3R^4$ = $(CH_2)_5$], selectively.
KD-80: Citing 3.



84) **Studies on organosilicon chemistry. 106. Ketene dithioacetals in organic synthesis: synthesis of silyl ketene dithioacetal and some reactions with substituted benzaldehydes.** Tominaga, Yoshinori; Matsuoka, Yoshiki; Kamio, Chizuko; Hosomi, Akira. *Chemical & Pharmaceutical Bulletin* (1989), 37(11), 3168-70. CODEN: CPBTAL ISSN:0009-2363. CAN 112:197727 AN 1990:197727 CAPLUS. **Abstract**-----$Me_3SiCH:C(SMe)_2$ (I) was prepd. in 4 steps from $Me_3SiCH_2Cl$ by sequential Grignard reaction with $CS_2$, methylation with MeI, lithiation, and methylation with MeI. Reaction of I with p-$RC_6H_4CHO$ (R = H, Me, Cl, cyano, $O_2N$) in the presence of $BF_3.OEt_2$ or $TiCl_4$ gave mainly p-$RC_6H_4CH(OH)CH:C(SMe)_2$.
KD-79: Citing 1.

85) **Studies in organosilicon chemistry. 100. Pentacoordinate allylsiliconates in organic synthesis: synthesis of triethylammonium bis(catecholato)allylsiliconates and selective allylation of aldehydes.** Hosomi, Akira; Kohra, Shinya; Ogata, Koichiro; Yanagi, Toshiharu; Tominaga, Yoshinori. *Journal of organic Chemistry* (1990), 55(8), 2415-20. CODEN:JOCEAH ISSN:0022-3263 CAN 112:179108 AN 1990:179108 CAPLUS. **Abstract**-----Pentacoordinate triethylammonium bis(catecholato)allylsiliconates were synthesized by reaction of allyltrialkoxysilanes, catechol, and $Et_3N$. The allylsiliconates react with aldehydes without catalyst to give the corresponding homoallyl alcs. in high yields in a completely regiospecific and highly diastereoselective mode. The stereochem. of the products can be reasonably interpreted by assuming a cyclic six-membered ring transition state. This allylation of aldehydes can also be effected by mixing them with an allyltrialkoxysilane, an alc., and an amine, generating the allylsiliconate in situ.
Citing 46.

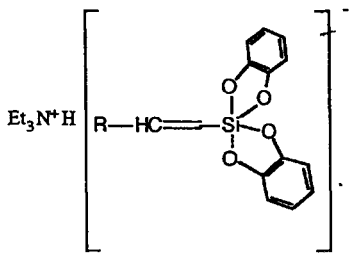
86) **Synthesis of heterocyclic compounds using carbon disulfide and their products.** Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1989), 26(5), 1167-204. CODEN: JHTCAD ISSN: 0022-152X. Journal; General Review written in English. CAN 112:178718 AN 1990:178718 CAPLUS. **Abstract**----A review with 139 refs. on developments in the synthesis of heterocyclic compds. using carbon disulfide and its products.
CS-47: Citing 50.

87) **New synthetic reactions using alkoxy-substituted highly coordinate organosilicon compounds.** Hosomi, Akira; Kohra, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yuki Gosei Kagaku Kyokaishi* (1989), 47(9), 831-42. CODEN: YGKKAE ISSN: 0037-9980. Journal; General Review written in Japanese. CAN 112:118877 AN 1990:118877 CAPLUS. **Abstract**----Synthesis and some reactions of highly coordinate organosilicon compds. as synthetic reagents, substituted by alkoxy groups, are reviewed with 38 refs. Topics are (1) prepns. of pentacoordinate allylsiliconates, (2) stereochem. outcomes of asym. allylation with optically active allylsiliconates, (3) cross-coupling reactions of alkenylsiliconates with org. iodides and triflates, and (4) chemo- and stereoselective redn. of carbonyl compds. using alkoxy-substituted hydrosiliconates and new catalytic asym. redn. of prochiral ketones using hydrosiliconates.
Citing 3.

88) **Synthesis of 2-pyrone and 2-pyridone derivatives using ketene dithioacetals.** Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yuki Gosei Kagaku Kyokaishi* (1989), 47(5), 413-24. CODEN: YGKKAE ISSN: 0037-9980. Journal; General Review written in Japanese. CAN 112:55461 AN 1990:55461 CAPLUS. **Abstract**----A review, with 88 refs., on recent developments in the synthesis of 2-pyrone and 2-pyridone derivs. by reaction of ketene dithio acetals with active Me or methylene compds. Reaction of 4-methylthio-2-pyridone or 2-pyridones with nucleophiles, such as amines and active methylene compds., is also described.
KD-78: Citing 14.

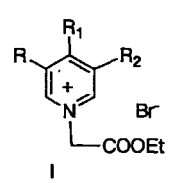
89) **Synthesis of pyrimidine derivatives and their related compounds using ketene dithioacetals.** Tominaga, Yoshinori; Kohra, Shinya; Honkawa, Harumasa; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1989), 29(7), 1409-29. CODEN: HTCYAM ISSN: 0385-5414. Journal; General Review written in English. CAN 112:7400 AN 1990:7400 CAPLUS. **Abstract**----A review with 87 refs.
KD-77: Citing 27.

90) **Studies on organosilicon chemistry. No. 96. Pentacoordinate organosilicon compounds in organic synthesis: cross-coupling of alkenylsiliconates with organic halides and triflates catalyzed by palladium complex.** Hosomi, Akira; Kohra, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1988), **36**(11), 4622-5. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 111:232959 AN 1989:632959 CAPLUS. **Abstract**----Pentacoordinate triethylammonium bis(catecholato)alkenyl- siliconates, e.g. I (R = H), readily prepd. from alkenyltrialkoxysilane, catechol, and Et3N, react with aryl iodides, vinylic iodides and aryl triflates catalyzed by a palladium complex to give the corresponding cross-coupled products in a stereospecific mode. Thus, reaction of I (R = H) with PhI in dioxane in the presence of $[PdCl(C_3H_5)]_2$ and $P(OEt)_3$ gave 30% $CH_2$:CHPh.
Citing 13.



I

91) **Synthesis of cycl[3.2.2]azine and benzo[*g*]cycl[3.2.2]azine derivatives by use of the [2 + 8] cycloaddition reaction of indolizines and dimethyl acetylenedicarboxylate.** Tominaga, Yoshinori; Shiroshita, Yoshihide; Kurokawa, Tomohiko; Gotou, Hiromi; Matsuda, Yoshiro; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1989), **26**(2), 477-87. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 111:194506 AN 1989:594506 CAPLUS. **Abstract**----The reaction of ethoxycarbonylmethylpyridinium bromides I (R = H, Me, Et, $CONH_2$, $CONEt_2$; $R^1$ = H, Et, Ac, $PhCH_2$; $R_2$ = H, Me) with $(MeS)_2C$:$CHNO_2$, in the presence of $Et_3N$ in EtOH gave the desired Et 2-methylthioindolizine-3-carboxylates II ($R^3$ = H, Me, COEt; $R^4$ = H, Et, $PhCH_2$; $R^5$ = H, Me, Et, $CONH_2$; $R^6$ = H) in good yields along with II ($R^3$ = H, $CONH_2$, $CONEt_2$; $R^4$ = H, Ac; $R^5$ = H, $R^6$ = $NO_2$). Deesterification of II ($R^6$ = H) with NaOH in MeOH followed by treatment with polyphosphoric acid gave the 2-methylthioindolizines III ($R^3$ = H, Me; $R^4$ = H, $PhCH_2$; $R^5$ = H, Me, Et) in good yields. The desulfurization of III with Raney-nickel in EtOH gave indolizine, 8-methylindolzine, 6,8-dimethylindolizine. Similarly, pyrrolo[2,1-*a*]isoquinoline (IV) was also synthesized. These indolizine and pyrrolo-[1,2-*a*]isoquinoline derivs. were allowed to react with $MeO_2CC$.tplbond.$CCO_2Me$ to give the corresponding cycl[3.2.2]azines, e.g., V, and benzo[*g*]cycl[3.2.2]azine derivs., e.g., VI.
KD-76: Citing 17.



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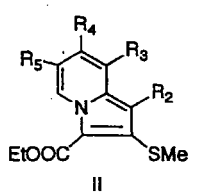
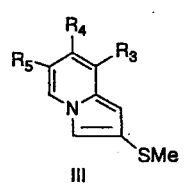
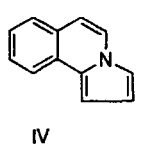


II



III



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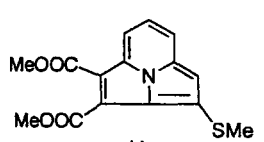

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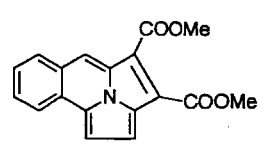
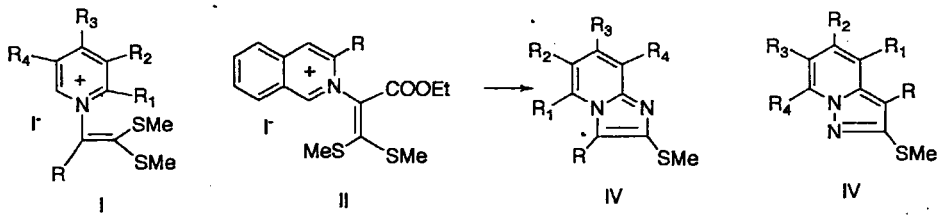


VI

92) **Studies on organosilicon chemistry. 98. Synthesis and consecutive double alkylation reactions of (2-siloxyallyl)silanes as the synthetic equivalent of acetone α,α'-dianion.** Hosomi, Akira; Hayashida, Hisashi; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Organic Chemistry* (1989), **54**(14), 3254-6. CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 111:57175 AN 1989:457175 CAPLUS. **Abstract**----2-Siloxy- allylsilanes $Me_3SiCH_2C(OSiMe_2R)$: $CH_2$ (I, R = Me, $CMe_3$), readily prepd. by quenching of an enolate of $Me_3SiCH_2COMe$ with chlorosilanes or by a 1, 3 CsF Si shift of $(Me_3SiCH_2)_2CO$ (II) catalyzed by $HgI_2$, consecutively react with various electro-

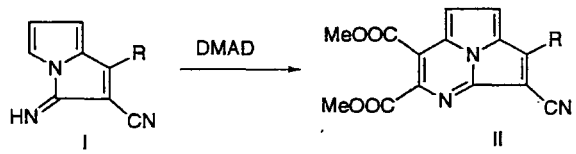
philes such as acetals and carbonyl compds. promoted by a Lewis acid to give the resp. α,α'-disubstituted acetones. Tandem aldol reactions using two electrophiles can be also achieved. II was also used as the reagent for the consecutive double alkylation. Thus, I and II are useful and convenient reagents as the synthetic equiv. of acetone α,α-dianion.
Citing 10.

93) **Nitroolefins. I. A new and convenient access to indolizines and pyrazolo[1,5-*a*]pyridines using 1-nitro-2-(phenylthio)ethylene.** Tominaga, Yoshinori; Ichihara, Yuichi; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Bunkyo, Japan. *Heterocycles* (1988), 27(10), 2345-8. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 111:39284 AN 1989:439284 CAPLUS. **Abstract**---1-Nitro-2-(phenylthio)ethylene reacts with a variety of N-ylides and *N*-imines (pyridinium, isoquinolinium, quinolinium, phthalazinium *N*-ylides and *N*-imines) in the presence of $Et_3N$ to give the corresponding fused pyrrole and pyrazole derivs. [indolizines I (R = H, $R^1$ = $CO_2Et$, CN, $R^2$ = H, Me), pyrrolo[2,1-*a*]isoquinoline, pyrrolo-[2,1-*a*]phthalazine (II, R= H), pyrazolo[1,5-*a*]pyridine, pyrazolo[5,1-*a*]quinoline, and pyrazolo[5,1-*a*]-isoquinoline], along with the corresponding 1-nitropyrrolopyridines and 1-nitropyrazolo- pyridines, e.g., I and II (R = $NO_2$), resp., in moderate yields.
KD-75: Citing 7.



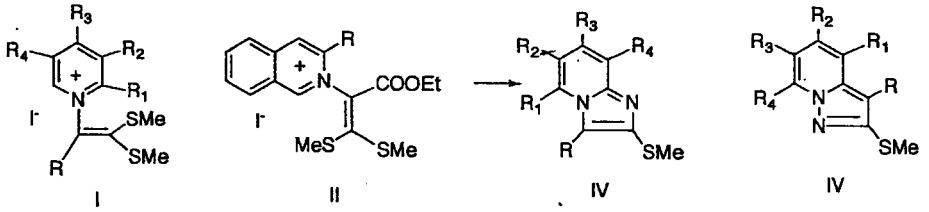

94) **Optically active allylsilanes. 14. Stereochemistry and mechanism of asymmetric allylation of aldehydes with optically active allylsiliconates.** Hayashi, Tamio; Matsumoto, Yonetatsu; Kiyoi, Takao; Ito, Yoshihiko; Kohra, Shinya; Tominaga, Yoshinori; Hosomi, Akira. Dep. Synth. Chem., Kyoto Univ., Kyoto, Japan. *Tetrahedron Letters* (1988), 29(44), 5667-70. CODEN: TELEAY ISSN: 0040-4039. Journal written in English. CAN 111:6979 AN 1989:406979 CAPLUS. **Abstract**----PhCHO reacted with (R)-(Z)-MeCH:CHCH($SiR_3$)Ph (I, R = EtO) in the presence of o-$(HO)_2C_6H_4$ and $Et_3N$ to give 27% (3S,4R)- and (3S,4S)-(E)-PhCH(OH)CHMeCH:CHPh in the ratio of 90:10, resp. The stereochem. of the products support a mechanism involving a 6-membered cyclic transition state. Allylation of PhCHO with I (R = F) also proceeded via this type of transition state.
Citing 24.

95) **A new synthesis of 5-aza[2.2.3]cyclazines by [8 + 2] cycloaddition of 3-imino-3*H*-pyrrolizines with dimethyl acetylenedicarboxylate.** Tominaga, Yoshinori; Matsuoka, Yoshiki; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1988), 27(12), 2791-4. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 110:231467 AN 1989:231467 CAPLUS. **Abstract**---- Cycloaddn. reaction of 3-imino-3*H*-pyrrolizines I (R = SMe, pyrrolidino, piperidino, morpholino), generated in situ, with di-Me acetylenedicarboxylate in the presence of Pd on charcoal in PhMe gave 23-72% 5-aza[2.2.3]cyclazine derivs. II.
Citing 1.

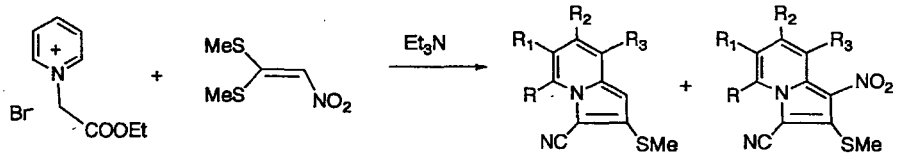



96) **Reactions of pyridinium or isoquinolinium ketene dithioacetals with aromatic *N*-imines and *S*-imines.** Tominaga, Yoshinori; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1988), 25(5), 1449-54. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 110:212678 AN 1989:212678 CAPLUS. **Abstract**----Reactions of ketene dithioacetals, 1-[1-substituted 2,2-bis(methylthio)ethenyl]pyridinium, e.g., I (R = $CO_2Et$; $R^1$-$R^4$ = H; $R^1$ = Me, $R^2$-$R^4$ = H; $R^1$ = $R^3$ = $R^4$ = H, $R^2$ = Me; $R^1$ = $R^2$ = $R^4$ = H, $R^3$ = Me; $R^1$ = $R^2$ = H, $R^3$ = $R^4$ = pre), or -isoquinolinium II ($R^5$ = H, Me) iodides with arom. *N*-imines, 1-aminopyridinium, 1-aminoquinolinium, and 2-aminoiso-

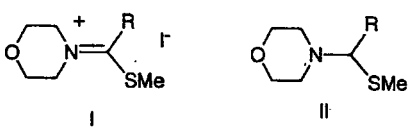
quinolinium mesitylenesulfonates gave the resp. 2-methylthioimidazo[1,2-*a*]pyridines III, 2-methylthiopyrazolo[1,5-*a*]pyridines IV, 2-methylthioimidazo[2,1-*a*]isoquinoline derivs. and 2-methylthiopyrazolo-[1,5-*a*]quinoline. The benzoyl compds., 1-[1-benzoyl-2,2-bis(methylthio)ethenyl]pyridinium iodides I (R =COPh) reacted with *N*-imine 1-amino- pyridinium mesitylenesulfonate to give the 3-benzoyl-2-methylthioimidazo[1,2-*a*]pyridines. The reaction of pyridinium ketene dithioacetals I (R = COOEt, COPh, CN) with substituted pyridinium *N*-imines having an electron-withdrawing group on the pyridine ring afforded only the resp. pyrazolo[1,5-*a*]pyridine derivs. in good yields. Reactions of ketene dithioacetals with various *S*-imines are also described. Possible mechanisms for the formation of III and IV are described.
KD-74: Citing 8.



97) **Synthesis of 2-methylthioindolizine-3-carbonitriles using nitroketene dithioacetal.** Tominaga, Yoshinori; Shiroshita, Yoshihide; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1988), 25(6), 1745-9. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 110:212542 AN 1989:212542 CAPLUS. **Abstract**—The reaction of 1-cyanomethyl- pyridinium chloride or bromide, with 1,1-bis(methylthio)-2-nitroethylene in the presence of $Et_3N$ in ethanol gave the corresponding 2-methylthio- indolizine-3-carbonitrile I (R = H, Ph; $R^1$ = H, Me, Et; $R^2$ = H, Et, Ph, $CH_2Ph$; $R^3$ = H, Me, Et) and 2-methylthio-1-nitroindolizine-3-carbonitrile in good yields, resp. Compds. I (R-$R^3$ = H; R = $R^2$ = H, $R^1$ = $R^3$ = Me) were key intermediates for the synthesis of cycl[3,2,2]azine derivs.
KD-73: Citing 8.

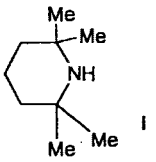


98) **Studies on organosilicon chemistry. 94. Highly coordinate organosilicon compounds in synthesis: new entry to *S,N*-acetals by selective reduction of alkylthiomethyleniminium salts by use of trimethoxysilane and dilithium 2,3-butanediolate.** Tominaga, Yoshinori; Matsuoka, Yoshiki; Hayashida, Hisashi; Kohra, Shinya; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Tetrahedron Letters* (1988), 29(45), 5771-4. CODEN: TELEAY ISSN: 0040-4039. Journal written in English. CAN 110:192748 AN 1989:192748 CAPLUS. **Abstract**—Redn. of alkylthiomethyleniminium iodides proceeds smoothly by use of $(MeO)_3SiH$ and dilithium 2,3-butanediolate in THF 0° to give the resp. *S,N*-acetals selectively in high yield. Thus, I (R = p-$MeOC_6H_4$, Ph, p-$Me_2NC_6H_4$), Bu, p-$ClCl_6H_4$, p-$NCC_6H_4$, p-$O_2NC_6H_4$, 2-thienyl, $R^1$ = Me; R = p-$MeOC_6H_4$, Ph, $R^1$ = Et) gave II in 36-98% yield.
Citing 6.



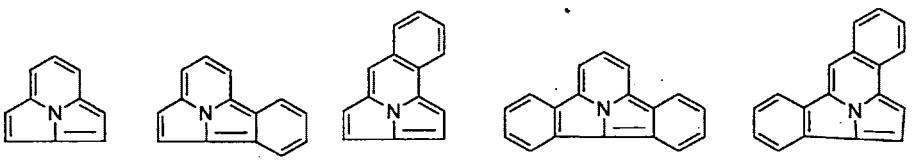
99) **A convenient synthesis of primary amines by *N*-alkylation of cyclic potassium disilylamides.** Hosomi, Akira; Kohra, Shinya; Tominaga, Yoshinori; Inaba, Masahiro; Sakurai, Hideki. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1988), 36(7), 2342-5. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 110:135321 AN 1989:135321 CAPLUS. **Abstract**—Potassium 2,6-disilapiperidide I (R = K) readily prepd. from 2,2,6,6-tetramethyl-2,6-disilapiperidine (I, R = H) and KH, can be smoothly *N*-alkylated with alkyl halides to give the corresponding

adducts I (R = Et, Pr, Bu, 1-octyl, $CH_2Ph$, $CH_2C_6H_4Me$-4). Acid hydrolysis of I (R = 1-octyl, $CH_2Ph$) gave the corresponding primary amines $RNH_2$ in 84 and 94% yields.
Citing 0.

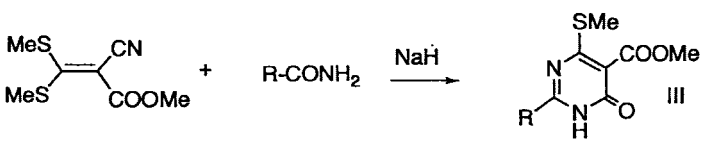


I

100) **Synthesis of [2.2.3]cyclazines, aza[2.2.3]cyclazines and their related compounds.** Tominaga, Yoshinori; Shiroshita, Yoshihide; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Bunkyo, Japan. *Heterocycles* (1988), 27(9), 2251-88. CODEN: HTCYAM ISSN: 0385-5414. Journal; General Review written in English. CAN 110:114707 AN 1989:114707-CAPLUS. **Abstract**----A review with 94 refs. on the recent developments in the synthesis of [2.2.3]cyclazines, benzo[*g*][2.2.3]cyclazines, benzo[*a*][2.2.3]-cyclazines, dibenzo[*a,h*][2.2.3]cyclazines, dibenzo[*a,g*][2.2.3]cyclazines, 1-aza[2.2.3]cyclazines, 5-aza-[2.2.3]cyclazines, and 1-azabenzo[*h*][2.2.3]cyclazines by the (8 + 2) cycloaddns. reaction of $MeO_2CC.tplbond.CCO_2Me$ with the various type indolizines. The synthesis of indolizines, imidazo-[1,2-*a*]pyridine, and their related compds. which are key intermediates for the synthesis of cyclazines is also described.
Citing 22.



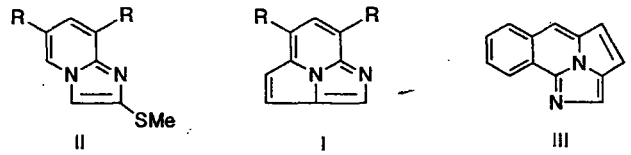
101) **Synthesis of pyrimidine derivatives by the reaction of ketene dithioacetals with amides.** Kohra, Shinya; Tominaga, Yoshinori; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1988), 25(3), 959-68. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 110:95143 AN 1989:95143 CAPLUS. **Abstract**---Reactions of Me 2-cyano-3,3-bis(methylthio)acrylate $(MeS)_2C{:}CRCN$ (I, R = $CO_2Me$) with carboxamides $R1CONH_2$(II, $R^1$ = 4-$R^2C_6H_4$, $ClCH_2$, Me, PhCH:CH; $R^2$ = H, $NO_2$, Me, MeO) in the presence of NaH gave the resp. Me 3-*N*-acylamino-2-cyano-3-(methylthio)acrylates $R^1CONaC(SMe){:}C(CO_2Me)CN$, which were readily converted to the resp. pyrimidine derivs. III (R = $CO_2Me$) at reflux in methanol in good yields. Reactions of 2-cyano-3,3-bis-(methylthio)acrylonitrile I (R = CN) with the carboxamides II gave directly pyrimidine-5-carbonitrile derivs. III (R = CN). Ketene dithioacetals smoothly reacted with thioacetamide or ureas to give the expected pyrimidine derivs. Polyfunctionalized pyrimidines, thus obtained, were also used for the synthesis of fused pyrimidine derivs.
KD-72: Citing 24.



III

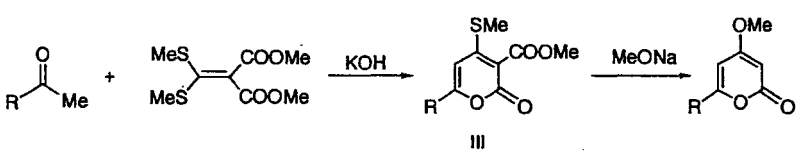
102) **Studies on organosilicon chemistry. 95. Novel arythiomethylation of carbonyl compounds using arythiomethyltrimethylsilanes catalyzed by fluoride ions. New route to β-hydroxy aryl sulfides.** Hosomi, Akira; Ogata, Koichiro; Hoashi, Koichiro; Kora, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan.*Chemical & Pharmaceutical Bulletin* (1988), 36(9), 3736-8. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 110:94112 AN 1989:94112 CAPLUS. **Abstract**----Arylthiomethyltrimethylsilanes $RSCH_2SiMe_3$ (R = Ph, m-tolyl) are good and mild nucleophilic reagents for introducing arylthiomethyl groups into carbonyl compds. $R^1R^2CO$ (arom. aldehydes, $PhCH_2CH_2CHO$, BuCHO, PhCOMe, cyclohexanone) promoted by tetra-n-butylammonium fluoride to give the corresponding β-hydroxyaryl sulfides $HOCR^1R^2CH_2SR$ in fairly good yields.
Citing 3.

103) **Synthesis of 1-azacycl[3.2.2]azine and 1-azabenzo[*h*]cycl[3.2.2]azine.** Tominaga, Yoshinori; Shiroshita, Yoshihide; Kurokawa, Tomohiko; Matsuda, Yoshiro; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1988), *25*(1), 185-9. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 109:210947 AN 1988:610947 CAPLUS. **Abstract**---- 1-Azacycl[3.2.2]azines I (R = H, Me) were synthesized from 2-methylthioimidazo[1,2-*a*]pyridines, II, by using [2 + 8] cycloaddn reaction with di-Me acetylenedicarboxylate as the key step. Synthesis of 1-azabenzo[*h*]cycl[3.2.2]azine (III) was also described.
KD-71: Citing 3.

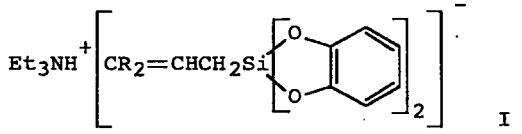



104) **Pentacoordinate organosilicon compounds in synthesis. Asymmetric reduction of carbonyl compounds with hydrosilanes catalyzed by chiral bases.** Kohra, Shinya; Hayashida, Hisashi; Tominaga, Yoshinori; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Tetrahedron Letters* (1988), 29(1), 89-92. CODEN: TELEAY ISSN: 0040-4039. Journal written in English. CAN 109:210615 AN 1988:610615 CAPLUS. **Abstract**----Asym. redn. of Ph ketones PhCOR (I, R = Me, Et, $CHMe_2$, Bu) with $HSi(OMe)_3$ in the presence of chiral bisalkoxides (S,S)- or (R,R)-$LiOCHR^1CHR^1OLi$ ($R^1$ = Me, $CH_2OMe$, $CH_2OCH_2Ph$, $CONMe_2$) gave the corresponding chiral alcs. (R)-PhCHROH in 41-78% yields and 22-69% enantiomeric excess (e.e.). Similar redn. of I in the presence of Li alkoxides from amino alcs. (S)-phenylalaninol, (S)-prolinol, (S)-valinol, and (S)-1,1-diphenylvalinol gave the corresponding (R)-alcs. in 12-100% yields and 12-84% e.e
Citing 31.

105) **Synthesis and reaction of 6-substituted 3-methoxycarbonyl-4-methylthio-2*H*-pyran-2-one derivatives.** Tominaga, Yoshinori; Ushirogochi, Atsuyuki; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1987), 24(6), 1557-67. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 109:54611 AN 1988:454611 CAPLUS. **Abstract**----RCOMe (e.g., R = Ph, 4-$MeOC_6H_4$, 3-pyridyl, 4-$MeOC_6H_4CH$:CH) reacted with $(MeS)_2C$:$C(CO_2Me)_2$ in the presence of KOH in $Me_2SO$ to give Me aryl- and styryl(methylthio)- oxopyrancarboxylates I (e.g., R = same as above, $R^1$ = MeS). I (R = Ph, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 3-pyridyl, etc.; $R^1$ = MeS) were treated with MeONa in MeOH to give arylmethoxypyranones II (R = same as above, $R^1$ = MeO) and I (R = 3-pyridyl, $R^1$ = MeO). Phenylcoumarin II (R = Ph, $R^1$ = H) and paracotoin (II; R = 4-$MeOC_6H_4$, $R^1$ = H) were prepd. by desulfurization of the corresponding II ($R^1$ = MeS). Nucleophilic substitution reactions of I ($R^1$ = MeSO) are also described.
KD-70: Citing 55.

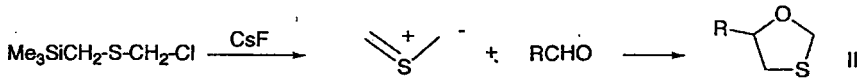



106) **Pentacoordinate silicon compounds in synthesis. Regiospecific allylation of aldehydes by use of triethylammonium bis(pyrocatecholato)allylsilicates.** Hosomi, Akira; Kohra, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of the Chemical Society, Chemical Communications* (1987), (20), 1517-18. CODEN: JCCCAT ISSN: 0022-4936, Journal written in English. CAN 108:221254 AN 1988:221254 CAPLUS. **Abstract**-----The title compds. I (R = H, Me), prepd. by reacting $CR_2$:$CHCH_2Si(OR^1)_3$ (R = H, Me, $R^1$ = Me, Et) with o-$(HO)_2C_6H_4$ in $Et_3N$, regioselectively allylated aldehydes under mild conditions, in the absence of a catalyst and even in protic solvents such as EtOH. Thus, PhCHO was treated with I (R = H) in $CH_2Cl_2$ for 20 h, followed by 1 M HCl and then 1 M NaOH to give 86% $CH_2$:$CHCR^2CH(OH)Ph$ (II; R = H). Similar treatment of PhCHO with I (R = Me) in $CHCl_3$ gave 72% II (R = Me).
Citing 27.



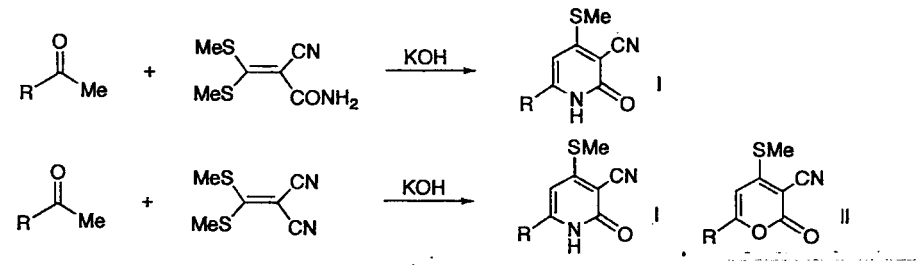
I

107) **Unprecedented reaction of a thiocarbonyl ylide with carbonyl compounds: a novel synthesis of 1,3-oxathiolanes.** Hosomi, Akira; Hayashi, Shinji; Hoashi, Koichiro; Kohra, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of the Chemical Society, Chemical Communications* (1987), (19), 1442-3. CODEN: JCCCAT ISSN: 0022-4936. Journal written in English. CAN 108:204532 AN 1988:204532 CAPLUS. **Abstract**----Thioformylium methylide, $H_2C{:}S{+}CH_2{-}$, generated from $Me_3SiCH_2SCH_2Cl$ (I) with CsF, underwent dipolar cycloaddn. reactions with arom. aldehydes, α-diketones, and α-oxoamides to give the corresponding 1,3-oxathiolanes in 35-86% yields. Thus, elimination and cycloaddn. of I with BzH gave 35% phenyloxathiolane II.
Citing 27.



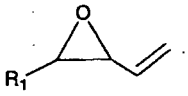
II

108) **Synthesis of 4-(methylthio)-2(1*H*)-pyridone derivatives using ketene dithio acetals.** Tominaga, Yoshinori; Kawabe, Masanori; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1987), 24(5), 1325-31. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 108:204458 AN 1988:204458 CAPLUS. **Abstract**----Reaction of active methylene compds. with ketene dithioacetals, $(MeS)_2C{:}C(CN)_2$ and $(MeS)_2C{:}C(CN)CONH_2$ gave cyanomethylthiopyridone I [R = Me, $CH_2CH_2CO_2H$, (un)substituted Ph; $R^1$ = H, Me, Ac, $CO_2Et$, $CH_2CO_2H$; $RR^1 = (CH_2)_4$]. The transformation of 4-methylthiooxopyrancarbonitriles II ($R^2$ = Ph, $C_6H_4Br$-4, $C_6H_4OMe$-4, Me, styryl) into I was also described.
KD-69: Citing 10.

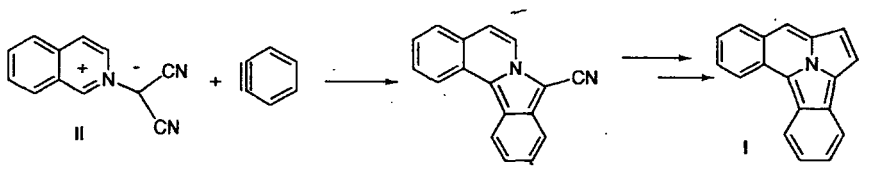


109) **A convenient and efficient metallation of methylsilane. Carbonyl methylenations using metallated (2-aminoalkoxy)trimethylsilane.** Hosomi, Akira; Kohra, Shinya; Tominaga, Yoshinori; Shoji, Masataka; Sakurai, Hideki. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan *Chemical & Pharmaceutical Bulletin* (1987), 35(4), 1663-5. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 108:167552 AN 1988:167552 CAPLUS. **Abstract**----When (2-aminoalkoxy)trimethylsilane is activated by two intramol. heteroatoms (oxygen and nitrogen), it undergoes metalation efficiently with $Me_2CLi$ to yield α-silyl carbanion. This process is applicable to carbonyl methylenations.
Citing 4.

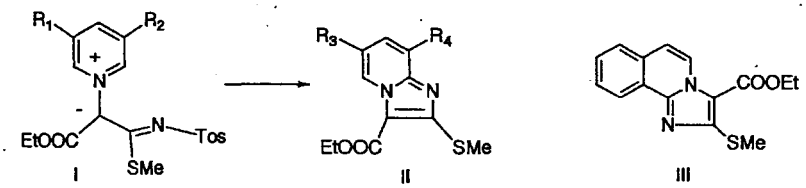
110) **Facile preparation of γ-chloro-substituted allylmetallic reagents and their reactions. Stereoselective access to cis-vinyloxiranes.** Hosomi, Akira; Kohra, Shinya; Tominaga, Yoshinori; Ando, Masatomo; Sakurai, Hideki. Fac. Pharm. Sci., Nagasaki Univ., Nagaski, Japan. *Chemical & Pharmaceutical Bulletin* (1987), 35(7), 3058-61. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 108:150171 AN 1988:150171 CAPLUS. **Abstract**----The title compds., e.g., (Z)-$ClCH{:}{=}CHCH_2SnR_3$ (R = Me, Bu), were readily prepd. from lithiated allyl chloride and $R_3SnCl$, $Et_2AlCl$ or $Ti(OCHMe_2)_4$. They react with $R^1CHO$ [$R^1$ = cyclohexyl, $Me_2CHCH_2$, $Me(CH_2)_3$, $Ph(CH_2)_2$, Ph] in highly regio- and diastereoselective modes, giving cis-vinyl oxiranes I ($R^1$ = as above).
Citing 6.



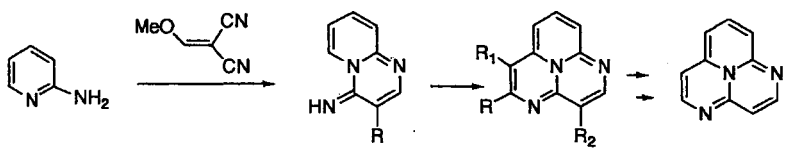
111) **The effect of benzannelation on cycl[3.2.2]azine. Synthesis and physical properties of dibenzo[*a,h*]cycl[3.2.2]azine.** Tominaga, Yoshinori; Shiroshita, Yoshihide; Matsuda, Yoshiro; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1987), 26(8), 2073-5. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 108:131559 AN 1988:131559 CAPLUS. **Abstract**——Dibenzo[*a,h*]cycl[3.2.2]azine (I) was prepd. by the cycloaddn. reaction of 1-cyanoisoindolo[2,1-*a*]isoquinoline (II) with benzyne and then with $MeO_2CC.tplbond.CCO_2Me$. The effect of dibenzoannelation on the six- and five-membered ring parts of the cyl[3.2.2]azine was examd.
Citing 9.



112) **A new synthesis of imidazo[1,2-*a*]pyridine and imidazo[2,1-*a*]isoquinoline derivatives.** Tominaga, Yoshinori; Motokawa, Shigenori; Shiroshita, Yoshihide; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1987), 24(5), 1365-9. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 108:112336 AN 1988:112336 CAPLUS. **Abstract**——Pyridinium (tosylimino)ethylides I ($R^1$ = H, Me; $R^2$ = H, Me) were heated in xylene to give imidazopyridines II ($R^3$ = H, Me, tosyl; $R^4$ = H, Me). Similarly prepd. were imidazoisoquinolines III ($R^5$ = Me, Et).
KD-68: Citing 12.

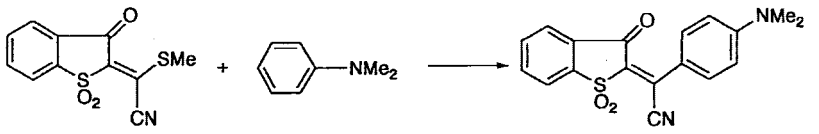


113) **Studies on quinolizine derivatives. XXI. The syntheses of cyclazine derivatives. (15).** Matsuda, Yoshiro; Tominaga, Yoshinori; Awaya, Hiroyoshi; Kurata, Keiji; Kato, Keisuke; Goto, Hiromi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1987), **107**(5), 344-9. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 108:56046 AN 1988:56046 CAPLUS. **Abstract**——Cycloaddn. of 4-imino-4*H*-pyridol[1,2-*a*]pyrimidine with RC. $tplbond.CCO_2Me$ (R= H, $CO_2Me$) with Pd-C as dehydrogenating reagent, gave 1,4-diazacycl[3.3.3]azines I (R = H, $CO_2Me$, $R^1$ = $CO_2Me$, $R_2$ = cyano). 1,4-Diazacycl[3.3.3]azine I (R = $R^1$ = $R^2$ = H) (II), which is a very unstable free base, was prepd. by the degrdn. of I (R = H, $R^1$ = $CO_2Me$, $R^2$ = cyano). The $^1H$ NMR of II was interpreted in terms of a paramagnetic ring current.
Citing 0.

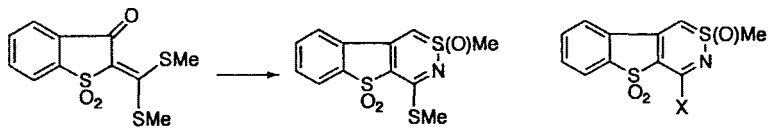


114) **Benzothiophene- or phthalic anhydride derivative dyes for organic polymers.** Matsuda, Yoshiro; Tominaga, Yoshinori; Maeda, Shuichi. (Mitsubishi Chemical Industries Co., Ltd., Japan). *Jpn. Kokai Tokkyo Koho* (1987), 5 pp. CODEN: JKXXAF JP 62185758 A 19870814 Showa. Patent written in Japanese. Application: JP 86-27445 19860210. Priority: CAN 108:39655 AN 1988:39655 CAPLUS. **Abstract**——The title dyes I [K = (un)substituted arom. amine residue, e.g., Q; R, $R^1$ = H, C1-20 (un)substituted alkyl, aryl, cyclohexyl; Y, Z = H, alkyl, acylamino, alkoxy, halogen; X = CO, $SO_2$] are prepd. and are useful for dyeing polyamide and polyester fibers and org. polymer films. Thus, I (K = SMe, X = $SO_2$) reacted with $PhNMe_2$ in AcOH under heating for 4 h to give 59% I (K = Q, R = $R^1$ = Me, X = $SO_2$, Y = Z = H), having max

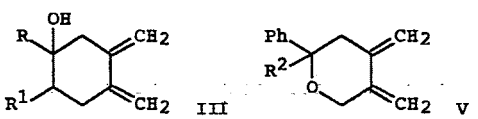
($CHCl_3$) 546 nm, which dyed polyester fibers in a fast purple shade.
Citing 0.



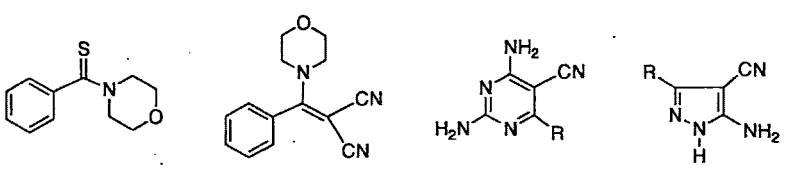
115) **Synthesis of thiabenzene oxides and azathiabenzene oxides.** Tominaga, Yoshinori; Hidaki, Shozo; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1987), 24(2), 519-20. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 108:21811 AN 1988:21811 CAPLUS. **Abstract**-----Thiazinobenzothiophenes I [$R^1$ = SMe, N:S(O)$Me_2$] were prepd. from benzothiophene deriv. II. II was treated with excess $Me_2S(O)$:NH, and the intermediate was treated with NaH to give I [$R^1$ = N:S(O)$Me_2$]. Thiopyranobenzothiophene III was prepd. from II, $Me_3S^+(O)$ $I^-$, and NaH.
KD-66: Citing 1.



116) **2-[(Dimethylamino)methyl]-3-[(trimethylsilyl)methyl-1,3-butadiene as a synthetic equivalent of 2,2'-biallyl zwitterionic species.** Hosomi, Akira; Hoashi, Koichiro; Kohra, Shinya; Tominaga, Yoshinori; Otaka, Ken; Sakurai, Hideki. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of the Chemical Society, Chemical Communications* (1987), (8), 570-1. CODEN: JCCCAT ISSN: 0022-4936. Journal written in English. CAN 108:21372 AN 1988:21372 CAPLUS. **Abstract**—*N*-Methylation of $Me_2NCH_2[C(:CH_2)]_2CH_2SiMe_3$ (I), followed by alkylation of enolates, e.g., $RCOCHNaCO_2R^1$ (R = OEt, Ph, $R^1$ = Et; R = $R^1$ = Me), in the presence of $Pd(PPh_3)_4$ gave intermediates e.g., $Me_3SiCH_2[C(:CH_2)]_2CH_2$-$CH(OR)CO_2R^1$ in 34-85% yields. Cyclization with catalytic $Bu_4NF$ (II) gave dimethylenecyclohexanols, e.g., III in 52-84% yields. Alkylation of ($R^2$ = Me, H) with I in the presence of II gave $Me_2NCH_2[C(:CH_2)]_2CH_2CR_2PhOH$ (IV) in 35 and 85% yields, resp. Reaction of IV with BrCN, followed by deprotonation and cyclization, gave dimethylenetetrahydropyrans V.
Citing 9.



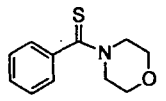
117) **A novel preparation of polarized ethylenes by the reaction of thioamides or dithiocarboxylates with tetracyanoethylene oxide. Synthesis of pyrazoles and pyrimidines.** Tominaga, Yoshinori; Matsuoka, Yoshiki; Kohra, Shinya; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1987), 26(3), 613-16. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 107:236648 AN 1987:636648 CAPLUS. **Abstract**-----Amides and esters $R^1C(S)R_2$ ($R^1$ = Ph, anisyl, $ClC_6H_4$, $PhCH_2$; $R^2$ = morpholino, SMe) were treated with tetracyanoethylene oxide to yield $R^1CR^2$:$C(CN)_2$, which reacted with guanidine to give pyrimidines I. Pyrazoles II were obtained from $R^1CR^2$:$C(CN)_2$ and $N_2H_4$.
Citing 10.



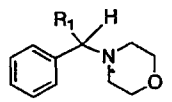
118) **Pentacoordinate silicon compounds in synthesis: regiospecific allylation of aldehydes using**

**trialkoxy-substituted allylsilane, pyrocatechol, and an amine.** Hosomi, Akira; Kohra, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1987), 35(5), 2155-7. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 107:236028 AN 1987:636028 CAPLUS. **Abstract**-----Allylating RCHO [R = Ph, PhCH:CH, Pr, $Me(CH_2)_6$, $R^1C_6H_4$; $R^1$ = 4-Me, 4-Cl, 3-$O_2N$] with $CH_2$:$CHCH_2Si(OEt)_3$ in the presence of o-$(HO)_2C_6H_4$ and $Et_3N$ gave 62-98% $CH_2$:$CHCH_2CHROH$. Similar reaction of $Me_2C$:$CHCH_2Si(OMe)_3$ with PhCHO gave 75% $CH_2$:$CHCMe_2CHPhOH$ as a single regioisomer.
Citing 5.

119) **Selective carbophilic addition of organolithiums to thioamides. A novel synthesis of unsymmetrical ketones and α-alkylated amines.** Tominaga, Yoshinori; Kohra, Shinya; Hosomi, Akira. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Tetrahedron Letters* (1987), 28(14), 1529-32. CODEN: TELEAY ISSN: 0040-4039. Journal written in English. CAN 107:198205 AN 1987:598205 CAPLUS. **Abstract**----Aryl ketones, e.g. $RCOR^1$ (R = Ph, 4-$ClC_6H_4$, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, $R^1$ = Me, Bu, Ph) were prepd. in 55-88% yield by addn. of R1Li to thioamides I followed by acidic hydrolysis. In a similar manner, α-alkylated amines II (R = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, $R^1$ = Bu, Ph) were prepd. by addn. of R1Li to the corresponding I, $LiAlH_4$ redn., and basic hydrolysis.
Citing 10.



I

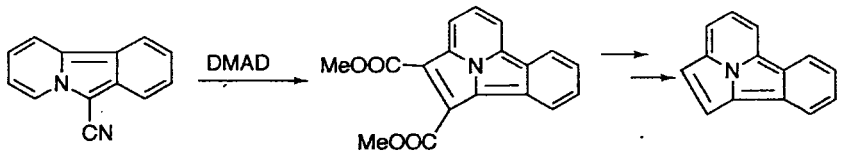


II

120) **Intramolecular cyclization via onium salts: a novel synthesis of 1,3-thiazolidines from chloromethyl (trimethylsilyl)methyl sulfide and nitrogen-containing heteroaromatic compounds.** Hosomi, Akira; Hayashi, Shinji; Hoashi, Koichiro; Kohra, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Organic Chemistry* (1987), 52(19), 4423-4. CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 107:198156 AN 1987:598156 CAPLUS. **Abstract**----A new and simple synthesis of 1,3-thiazolidines, e.g., I, is attained by the novel intramol. cyclization of the onium salts II (R-$R^4$ = H; $RR^1$, $R^2R^3$ = CH:CHCH:CH), readily prepd. from $Me_3SiCH_2SCH_2Cl$ and nitrogen-contg. heteroarom. compds. (pyridine, quinoline, phenanthridine, etc.), promoted by CsF in MeCN at room temp. This provides the 1st example of the introduction of a thiocarbonyl ylide synthon to heteroaroms.
Citing 7.

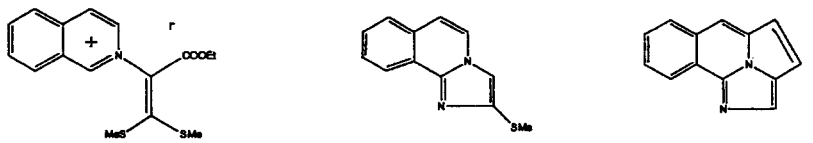

121) **A novel synthesis of 3-alkyl-substituted isoprenylsilanes.** Hosomi, Akira; Hoashi, Koichiro; Tominaga, Yoshinori; Otaka, Ken; Sakurai, Hideki. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Organic Chemistry* (1987), 52(13), 2947-8. CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 107:23393 AN 1987:423393 CAPLUS. **Abstract**----The cross-coupling reaction of RMgX (R = Bu, $PhCH_2$, $Me_3SiCH_2$; X = Cl, Br) with $Me_3SiCH_2C(:CH_2)C(:CH_2)CH_2N{+}Me_2R^1$ (X1)- ($R^1$ = Me, Bu, $PhCH_2$; X1 = Cl, iodo), catalyzed by dilithium tetrachlorocuprate, gave good yields of the title compds. $Me_3SiCH_2C(:CH_2)C(:CH_2)CH_2R$.
Citing 0.

122) **Synthesis of benzannelated cycl[3.2.2]azine: benzo[*a*]cycl[3.2.2]azine.** Tominaga, Yoshinori; Shiroshita, Yoshihide; Gotou, Hiromi; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1986), 24(11), 3071-4. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 106:213901 AN 1987:213901 CAPLUS. **Abstract**----The title azine I ( R = H) was prepd. from benzindolizine II in three steps. The key reaction was a [12 + 2] cycloaddn. reaction of II with $MeO_2CC.tplbond.CCO_2Me$ to give I (R = $CO_2Me$) in 54% yield.
Citing 8.

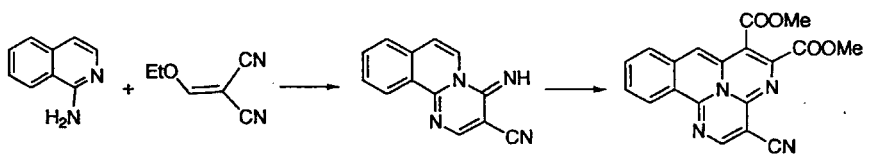



123) **Pentacoordinate silicon compounds in synthesis: chemo- and stereo-selective reduction of carbonyl compounds using trialkoxy-substituted silanes and alkali metal alkoxides.** Hosomi, Akira; Hayashida, Hisashi; Kohra, Shinya; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of the Chemical Society, Chemical Communications* (1986), (18), 1411-12. CODEN: JCCCAT ISSN: 0022-4936. Journal written in English. CAN 106:195541 AN 1987:195541 CAPLUS. **Abstract**---- Carbonyl compds. were reduced to the corresponding alcs. by title systems [e.g., $HSi(OMe)_3$ and LiOMe or $LiOCMe_2CMe_2OLi$] in $Et_2O$ at room temp. Carbonyl compds. reduced by this method include BzH, octanal, 2-tetralone, and cyclohexanone.
Citing 20.

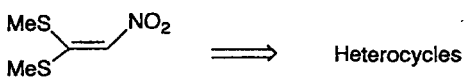
124) **Synthesis of benzannelated 1-azacycl[3.2.2]azine: 1-azabenzo[h]cycl[3.2.2]azine.** Tominaga, Yoshinori; Shiroshita, Yoshihide; Kawabe, Masanori; Goto, Hiromi; Oniyama, Yukio; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1985), 23(10), 2531-4. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 105:114970 AN 1986:514970 CAPLUS **Abstract**---- Azabenzocyclazine I was prepd. by cyclocondensation of vinylisoquinoline II and amino- pyridinium mesitylenesulfonate to yield imidazoisoquinoline III. Subsequent decarboxylation, cycloaddn. with $MeO_2CC.tplbond.CCO_2Me$, didecarboxylation, and sulfur cleavage produced I.
KD-65: Citing 3.




125) **Studies on quinolizine derivatives XVIII. Syntheses of azabenzocycl[3.3.3]azine derivatives.** Kurata, Keiji; Awaya, Hiroyoshi; Gotou, Hiromi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1985), 33(7), 3034-7. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 105:97411 AN 1986:497411 CAPLUS. **Abstract**----Azabenzocyclazines I and II were synthesized by reaction of $MeO_2CC.tpl-bond.CCO_2Me$ (III) with iminoisoquinolino[1,2-*a*]pyrimidine IV (X = N). Benzocyclazine V was prepd. by reaction of III with IV (X = $CCO_2Me$).
Citing 3.

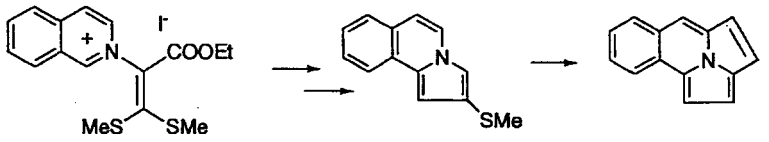



126) **Synthesis of heterocyclic compounds using nitro ketene dithioacetal.** Tominaga, Yoshinori; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Heterocyclic Chemistry* (1985), 22(4), 937-49. CODEN: JHTCAD ISSN: 0022-152X. Journal; General Review written in English. CAN 105:6417 AN 1986:406417 CAPLUS. **Abstract**----A review with 167 refs., which describes the synthesis of heterocyclic compds. using the nitro ketene dithioacetal $(MeS)_2C:CHNO_2$.
KD-64: Citing 36.

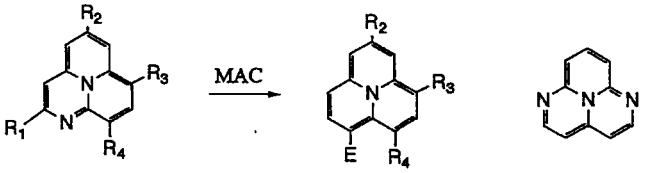



127) **Synthesis of benzannelated cycl[3.2.2]azine: benzo[g]cycl[3.2.2]azine.** Tominaga, Yoshinori; Gotou, Hiromi; Oniyama, Yukio; Nishimura, Yuko; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1985), 33(7), 3038-41. CODEN: CPBTAL ISSN: 0009-2363.

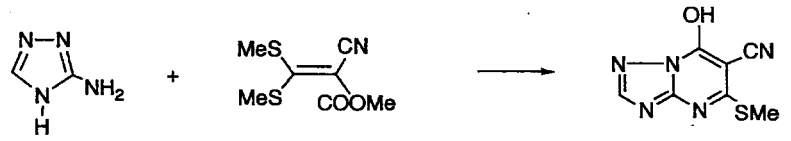
Journal written in English. CAN 104:207122 AN 1986:207122 CAPLUS. **Abstract**---Benzo-[*g*]cycl[3.2.2]azine (I) was synthesized from 2-(methylthio)pyrrolo[2,1-*a*]isoquinoline (II) and $MeO_2CC.tplbond.CCO_2Me$. The key intermediate II for I synthesis was prepd. in good yield by treating isoquinolinium ketene dithioacetal III with $MeNO_2$. III was obtained by reacting 2-[(ethoxy-carbonyl)methyl]isoquinolinium bromide with $CS_2$ and $Me_2SO_4$ in the presence of NaOH, followed by methylation with MeI.
KD-63: Citing 43.




128) **Studies on quinolizine derivatives. 20. Syntheses of cyclic [3.3.3]azine derivatives.** Gotou, Hiroma; Kurata, Keiji; Tominaga, Yoshinori; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Journal of Organic Chemistry* (1985), **50**(21), 4028-32. CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 103:196050 AN 1985:596050 CAPLUS. **Abstract**---Diels-Alder reactions of azacyclazine I (R = H, Me, $R^1$ = H, $R^2$ = $CO_2Me$, $R^3$ = cyano; R = Me, $R^1$ = H, Me, $R^2$ = $CO_2Me$, $R^3$ = $CO_2Et$; R = Me, $R^1$ = H, $R^2$ = cyano, $R^3$ = $CO_2Et$) with $HC.tplbond.CCO_2Me$ in MeCN gave cyclazines II and III ($R^4$ = $CO_2Me$, $R^5$ = H), while reactions of I (R = H, Me, $R^1$ = H, $R^2$ = $CO_2Me$, $R^3$ = cyano; R = $R^1$ = Me, $R^2$ = $CO_2Me$, $R^3$ = cyano; R = Me, $R^1$ = H, $R^2$ = $CO_2Me$, $R^3$ = $CO_2Et$) with $MeO_2CC.tplbond.CCO_2Me$ in DMF gave III ($R^4$ = $R^5$ = $CO_2Me$). I (R = Me, $R^1$ = H, $R^2$ = $CO_2Me$, $R^3$ = $CO_2Et$) treated with *N*-phenylmaleimide in DMF gave azacyclazine IV. Triazacyclazine V treated with $MeO_2CC.tpl-bond.CCO_2Me$ in DMF gave diazacyclazine VI ($R^6$ = $R^7$ = $CO_2Me$, $R^8$ = cyano, $R^9$ = H), whereas in MeCN V gave VI ($R^6$-$R^9$ = $CO_2Me$). The latter compd. was treated with 48% HBr to give VI-HBr ($R^6$-$R^9$ = H). The $H^1$ NMR of the free base may be interpreted in terms of a paramagnetic ring current.
Citing 4.

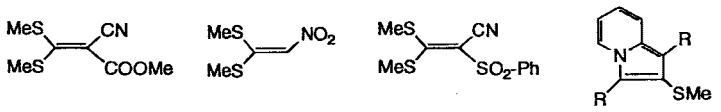



129) **Pyrimidine and fused pyrimidine derivatives. III. Synthesis of s-triazolo[1,5-*a*]pyrimidine derivatives by using ketene dithioacetals.** Tominaga, Yoshinori; Sakai, Shuichiro; Kohra, Shinya; Tsuka, Junko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1985), **33**(3), 962-70. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 103:123428 AN 1985:523428 CAPLUS **Abstract**---Cyclocondensation of triazolamine I with ketene dithioacetals, e.g. $(MeS)_2C:C(CN)CO_2Me$ gave triazolopyrimidines, e.g. II (R = SMe)(III). Amination of III gave the 7-(un)substituted amino derivs., e.g. II (R = $NH_2$, NHPh, $NEt_2$, morpholino, etc.).
KD-62: Citing 10.

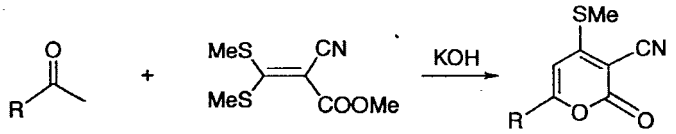



130) **Synthesis of indolizine derivatives and their related compounds using ketene dithioacetals.** Tominaga, Yoshinori; Matsuda, Yoshiro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yuki Gosei Kagaku Kyokaishi* (1985), **43**(7), 669-79. CODEN: YGKKAE ISSN: 0372-770X. Journal; General Review written in Japanese. CAN 103:123276 AN 1985:523276 CAPLUS. **Abstract**---The synthesis of indolizine derivs. by 1,5-dipolar cyclization, the reaction of picolinium salts with ketene dithioacetals, the reaction of 2-pyridyl ketene dithioacetals with α-halocarbonyl compds., the reaction of pyridinium or isoquinolinium ketene dithioacetals, or the reaction of *N*-imines or *S*-imines with ketene dithioacetals are reviewed with 97 refs.

KD-61: Citing 18.

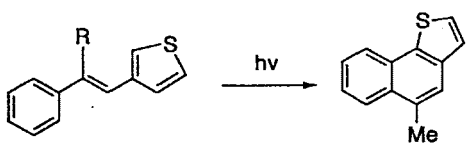


131) **Synthesis and reactions of 6-aryl- and 6-styryl-3-cyano-4-methylthio-2*H*-pyran-2-ones.** Tominaga, Yoshinori; Ushirogochi, Atsuyuki; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1984), 32(9), 3384-95. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 102:95499 AN 1985:95499 CAPLUS. **Abstract**---The reaction of various types of acetyl compds. with a ketene dithioacetal, Me 2-cyano-3,3-bis-(methylthio)-acrylate, in the presence of KOH gave the corresponding 6-aryl- and 6-styryl-3-cyano-4-methyl-thio-2*H*-pyran-2-one derivs., e.g. I. The methylthio group on the pyrone ring reacted readily with nucleophiles such as amines, active methylene compds. and methoxy anion to yield the corresponding displacement products in good yields.
KD-60: Citing 43.



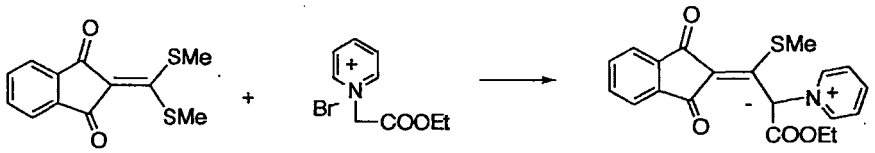
132) **Capillary column gas chromatography of sulfur heterocycles in heavy oils and tars using a biphenyl polysiloxane stationary phase.** Nishioka, Masaharu; Bradshaw, Jerald S.; Lee, Milton L.; Tominaga, Yoshinori; Tedjamulia, Marvin; Castle, Raymond N. Dep. Chem., Brigham Young Univ., Provo, UT, USA. *Analytical Chemistry* (1985), 57(1), 309-12. CODEN: ANCHAM ISSN: 0003-2700. Journal written in English. CAN 102:27859 AN 1985:27859 CAPLUS. **Abstract**---A newly synthesized biphenylyl Me siloxane is a selective stationary phase for the sepn. of isomeric S heterocycles by capillary-column gas chromatog. In conjunction with flame photometric detection, the S heterocycles in various heavy oils and tars were detd. Anthra[2,3-*b*]thiophene [22108-55-0], phenaleno[6,7-*bc*]thiophene [79965-99-4], and 2-methylphenanthro[4,5-*bcd*]thiophene [88114-00-5] were identified for the first time in these materials.
Thiophene-18: Citing 8.

133) **The synthesis of naphtho[1,2-*b*]thiophene and all of the eight isomers of monomethyl-naphtho[1,2-*b*]thiophene.** Tedjamulia, Marvin L.; Stuart, John G.; Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1984), 21(4), 1215-19. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 102:24403 AN 1985:24403 CAPLUS. **Abstract**---The synthesis of naphtho[1,2-*b*]thiophene and all of the eight monomethylnaphtho[1,2-*b*]thiophene isomers is described. E.g., condensation of 2-$MeC_6H_4CHO$ with di-Et 3-thenylphosphonate followed by photocyclization gave naphthothiophene I.
Thiophene-17: Citing 3.

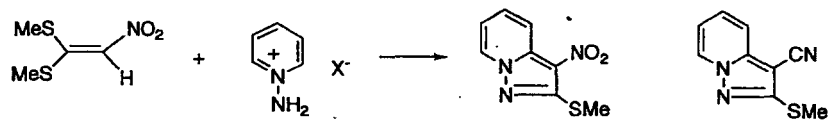


134) **Reaction of 2-[bis(methylthio)methylene]indan-1,3-dione with *N*-ylides and *S*-ylides.** Tominaga, Yoshinori; Norisue, Hajime; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1984), 32(8), 2910-14. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 102:6390 AN 1985:6390 CAPLUS. **Abstract**---The reaction of the title compd. (I) with pyridinium *N*-ylides II (R = H, 3-Me, 2-Me, 2-NH2) gave the corresponding stable pyridinium *N*-allylides III (R=H, Me), 2-(2-indanyl)indolizine, and 3-(2-indanylidenyl)methyl-imidazo[1,2-*a*]pyridine in good yields. A fused thiabenzene oxide, 2-methyl-4-methylthio-5-oxo-5*H*-indeno[1,2-c]thiapyran 2-oxide, was synthesized by the reaction of I with trimethylsulfoxonium iodide under similar conditions. An azathiabenzene oxide, 2-methyl- 4-methylthio-5-oxo-5*H*-indeno[2,1-*d*][1,2]thiazine 2-oxide was also synthesized from 2-(1-dimethyl-sulfoximino-1-methylthio)methyleneindan-1,3-dione,

which was prepd. from I and sulfoximine.
KD-59: Citing 3.

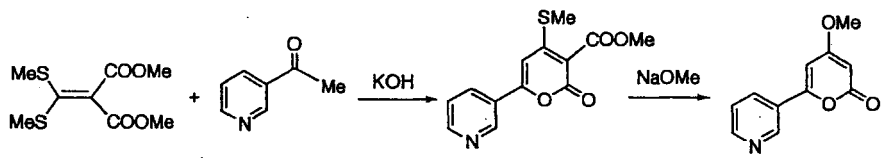


135) **Reaction of pyridinium and quinolinium *N*-imines with ketene thioacetals.** Tominaga, Yoshinori; Hidaki, Shozo; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1984), ***104***(5), 440-8. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 102:6281 AN 1985:6281 CAPLUS. **Abstract**—Reaction of 1-aminopyridinium and 1-aminoquinolinium mesitylenesulfonates (I; R = H, RR = benzo; $R^1$ = H, Me, cyano, etc., $R^2$ = H, Me, $H_2NCO$; X = mesitylenesulfonate) with $(MeS)_2C{:}C(CN)_2$, $(MeS)_2C{:}CHNO_2$, and $(MeS)_2C{:}CXSO_2C_6H_4R^3$-p ($R^3$ = H, Me; X = cyano, $EtO_2C$, Ac) gave *N*-substituted (1-pyridinio)amides, (1-quinolinio)amide, pyrazolo-[1,5-*a*]pyridines and pyrazolo[1,5-*a*]quinolines II ($R^4$ = H, Me; $R^5$ = H, Me, $H_2NCO$, cyano, etc.; $R^6$ = $O_2N$, cyano, $EtO_2C$, Ac; $R^7$ = MeS, cyano) in good yield. I also reacted with $MeSC(CN){:}C(CN)SO_2Ph$ to give II (RR = benzo, $R^4$ = $R^5$ = H, $R^6$ = $R^7$ = cyano) in good yield.
KD-58: Citing 4.

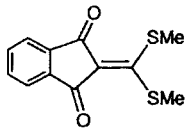
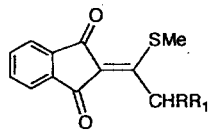
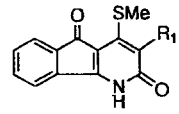


136) **The synthesis and properties of polycyclic aromatic thiophenes and related heterocycles occurring in coal-derived products.** Castle, Raymond N.; Tedjamulia, Marvin L.; Tominaga, Yoshinori; Pratap, Ram; Sugiura, Michiharu; Kudo, Hirotaka; Lee, Milton L.; Iwao, Masatomo; Thompson, Robert D.; et al. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Lectures in Heterocyclic Chemistry* (1984), 7, 1-52. CODEN: LHCHD2 ISSN: 0090-2268. Journal; General Review written in English. CAN 101:210877 AN 1984:610877 CAPLUS. **Abstract**—A review with 126 refs.
Thiophene-17.

137) **Synthesis of anibine using ketene dithioacetal.** Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1984), **32**(4), 1665-6. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 101:152151 AN 1984:552151 CAPLUS. **Abstract**—3-Acetylpyridine was cyclized with $(MeS)_2C{:}C(CO_2Me)_2$ to give the pyridylpyrancarboxylate I which underwent substitution with MeONa followed by treatment with polyphosphoric acid to give anibine (II).
KD-57: Citing 10.

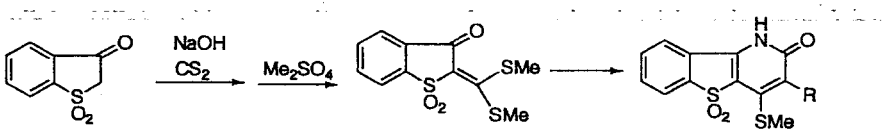


138) **Reaction of 2-bis(methylthio)methylene-1,3-indandione with active methylene compounds.** Tominaga, Yoshinori; Norisue, Hajime; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1984), **104**(2), 127-33. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 101:90510 AN 1984:490510 CAPLUS. **Abstract**—Reaction of the indandione I with active methylene compds. $RCH_2R^1$ (R, $R^1$ = cyano, $CO_2Me$; cyano, cyano; cyano, Ph; $CO_2Me$, $CO_2Me$; $CO_2Et$, Ph; COMe, COMe; COMe, $CO_2Me$) in DMF contg. $K_2CO$ gave in good yields the corresponding displacement products II of 1 MeS group. II (R = cyano, $R^1$ = $CO_2Me$, cyano, Ph) underwent intramol. cyclocondensation to give the corresponding indenopyridines III.
KD-56: Citing 2.

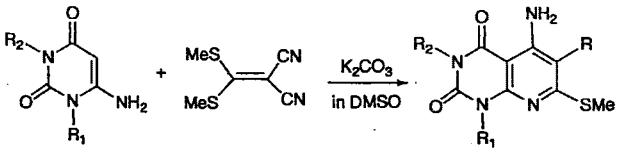




139) **Determination of sulfur heterocycles in selected synfuels.** Kong, Robert C.; Lee, Milton L.; Iwao, Masatomo; Tominaga, Yoshinori; Pratap, Ram; Thompson, Robert D.; Castle, Raymond N. Dep. Chem., Brigham Young Univ., Provo,UT, USA. *Fuel* (1984), **63**(5), 702-8. CODEN: FUELAC ISSN: 0016-2361. Journal written in English. CAN 101:40783 AN 1984:440783 CAPLUS. **Abstract**---A fractionation method for isolating polycyclic arom. S heterocycles from complex mixts. of polycyclic arom. compds. was evaluated with respect to recovery for 8 std. compds. The method consisted of oxidn. of the S compds. with $H_2O_2$ to the corresponding sulfones, which were sepd. from unoxidized compds. by silica gel adsorption chromatog. The sepd. sulfones were then reduced with $LiAlH_4$ back to the original S compds. and sepd. from hydroquinones (formed by redn. of oxidized polycyclic arom. compds.) by a 2nd silica gel chromatog. adsorption. Recovery varied from 0-70%, depending on the structure of the compd. Although quant. recovery for all components was not obtained, isolation of the S heterocycle fractions has allowed the identification of many new S compds. previously not identified in coal liqs. and shale oils. Capillary column gas chromatog. with flame photometric detection and mass spectrometry were used for the identification of individual S heterocycles.
Thiophene-16: Citing 4.

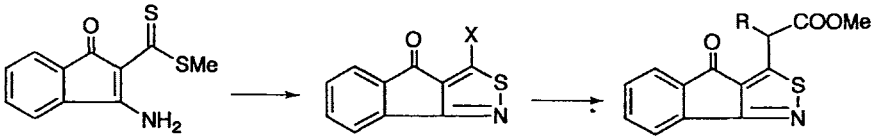
140) **Sulfonyl ketene thioacetal. V. Synthesis and reaction of 2,3-dihydro-2-bis(methylthio)-methylene-3-oxobenzo[*b*]thiophene 1,1-dioxide.** Tominaga, Yoshinori; Hidaki, Shozo; Matsuda, Yoshiro; Kobayashi, Goro; Sakemi, Kanro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1984), **104**(2), 134-41. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 101:23255 AN 1984:423255 CAPLUS. **Abstract**---The title compd. (I) was obtained by the reaction of 2,3-dihydro-3-oxobenzo[*b*]thiophene 1,1-dioxide with $CS_2$ in the presence of NaOH in $Me_2SO$ followed by treatment with Me iodide. The reaction of I with various amines gave the corresponding amine derivs. and heterocyclic compds. (imidazoline, hexahydropyrimidine, oxazoline, benzimidazoline, quinazoline, and thiazoline). The reaction of I with active methylene compds. gave the displacement products of a methylthio group and the heterocyclic compds., benzothienol[3,2-*b*]pyridine derivs. II (R = $MeO_2C$, $PhSO_2$, $MeSO_2$), in good yields. Similarly, the reaction of I with enamines afforded a good yield of corresponding displacement products. The reaction of I with sodium cyanide in di-Me sulfoxide gave 2-(1-cyano-1-methylthio)-methylene-2,3-dihydro-3-oxobenzo[*b*]thiophene 1,1-dioxide (III) in good yield. The reaction of III with aniline or *N,N*-dimethylaniline also gave the corresponding displacement products of methylthio group in good yields.
CS-45: KD-55: Citing 5.



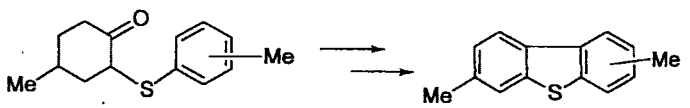

141) **Reactions of 6-aminouracils with ketene thioacetals.** Tominaga, Yoshinori; Kohra, Shinya; Okuda, Hiroto; Ushirogochi, Atsuyuki; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1984), **32**(1), 122-9. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 100:209737 AN 1984:209737 CAPLUS. **Abstract**---Reaction of $(MeS)_2C{:}CRCN$ (R = $CO_2Me$, $SO_2Ph$) with 6-aminouracils in the presence of $K_2CO_3$, followed by cyclization under reflux in $Ph_2O$ gave the 5-amino-6-methoxycarbonyl-7-methylthiopyrido[2,3-*d*]-pyrimidine-2,4(1*H*,3*H*)-dione derivs. I (R = $CO_2Me$, $SO_2Ph$; $R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = H$). Reaction of other ketenethioacetals with 6-aminouracils directly afforded pyrido[2,3-*d*]pyrimidine derivs. in good yields. 5-Amino-7-methylthiopyrimido[4,5-*d*]pyrimdine-2,4(1*H*,3*H*)-dione derivs. were similarly synthesized from 6-aminouracils and $(MeS)_2C{:}NCN$.
KD-54: Citing 13.



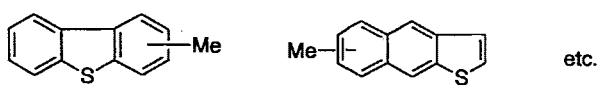
142) **Synthesis and reactions of methyl 1,3-dioxoindan-2-dithiocarboxylate.** Tominaga, Yoshinori; Norisue, Hajime; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1983), **103**(12), 1243-6. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 100:209677 AN 1984:209677 CAPLUS. **Abstract**---The reaction of indan-1,3-dione with $CS_2$ followed by methylation with $Me_2SO_4$ or MeI in the presence of NaOH gave 2-[bis(methylthio) methylene]indan-1,3-dione, 2-[mercapto(methylthio)methylene]-indan-1,3-dione (I), and 2,5-bis[1,3-dioxo-2-indanylidene]-1,3,5-trithiolane. I reacted with $NH_3$ to give Me 3-amino-1-oxoindan- 2-dithiocarboxylate which was converted to 8-methylthioindeno[2,1-*c*]isothiazol-3(3*H*)-one (II) by the treatment with iodine in $Me_2SO$. II reacted with RH (R = morpholino, piperidino) and $R^1CHCO_2Me$ ($R^1$ = cyano, $CO_2Me$) to give indenoisothiazolinones III and IV, resp.
CS-44: Citing 2.



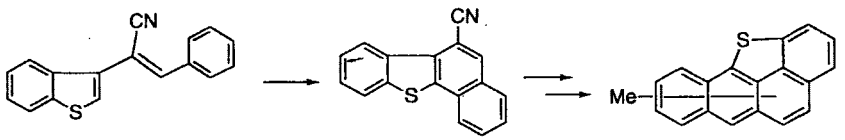
143) **The synthesis of all of the dimethyldibenzothiophenes and monoethyldibenzothiophenes.** Tedjamulia, Marvin L.; Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1983), **20**(6), 1485-95. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 100:191683 AN 1984:191683 CAPLUS. **Abstract**---The synthesis of all four isomers of the monoethyldibenzothiophenes I and all of the sixteen isomers of the dimethyldibenzothiophenes II has been accomplished. Thus, alkylation of 2-$MeC_6H_4SH$ by 2-bromo-4-methylcyclohexanone gave sulfide III which underwent cyclization in refluxing $C_6H_6$ contg. polyphosphoric acid and then Se catalyzed dehydrogenation to give dibenzothiophene IV.
Thiophene-15: Citing 11.



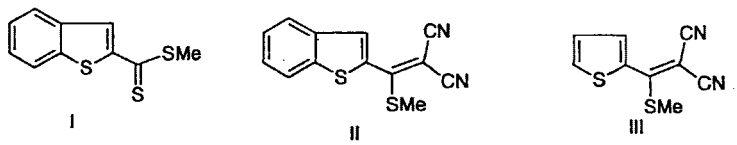
144) **Mutagenic activity of methyl-substituted tri- and tetracyclic aromatic sulfur heterocycles.** McFall, Teri; Booth, Gary M.; Lee, Milton L.; Tominaga, Yoshinori; Pratap, Ram; Tedjamulia, Marvin; Castle, Raymond N. Dep. Zool., Brigham Young Univ., Provo, UT, USA. *Mutation Research* (1984), **135**(2), 97-103. CODEN: MUREAV ISSN: 0027-5107. Journal written in English. CAN 100:187029 AN 1984:187029 CAPLUS. **Abstract**---The mutagenic activity of some polycyclic arom. S heterocycles identified in coal-derived products and in shale oils, including dibenzothiophene (I) [132-65-0], benzo[*b*]naphtha-[1,2-*d*]thiophene [205-43-6], benzo[*b*]naphtho[2,1-*d*]thiophene [239-35-0], and benzo[b]naphtha-[2,3-*d*]thiophene [243-46-9], was detd. using the Salmonella/microsome mutagenicity test. These compds. demonstrated either very weak or no mutagenic activity. The Me derivs. of each of these 4 compds. were assayed for mutagenic activity. S. typhimurium TA98 was used as the tester strain. All assays required a rat-liver homogenate metabolic activator. Five of the methylated derivs., 1-methylbenzo[*b*]naphtho[1,2-*d*]-thiophene [84258-62-8], 3-methylbenzo[b]naphtho[1,2-*d*]thiophene [84258-63-9], 1-methylbenzo[*b*]-naphtho[2,1-*d*]thiophene [4567-41-3], 6-methylbenzo[*b*]naphtha[2,1-*d*]thiophene [4567-51-5], and 4-methylbenzo[*b*]naphtho[2,3-*d*]thiophene [36821-08-6], demonstrated mutagenic activity. However, activity was obsd. only at high concns. of the metabolic activator.
Thiophene-14: Citing 1.



145) **The synthesis of the monomethylbenzo[2,3]phenanthro[4,5-*bcd*]thiophenes.** Sugiura, Michiharu; Tedjamulia, Marvin L.; Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL,U SA *Journal of Heterocyclic Chemistry* (1983), 20(6), 1453-9. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 100:174576 AN 1984:174576 CAPLUS. **Abstract**---The synthesis of the potentially mutagenic benzo[2,3]phenanthro[4,5-*bcd*]thiophenes I (R = 1-Me, 3-Me, 4-Me, 5-Me, 7-Me, 8-Me, 9-Me, 10-Me) is reported. Thus, condensation of 3-(cyanomethyl)-benzo[b]thiophene with BzH gave the nitrile II which underwent photochem. cyclization to give naphthobenzothiophene III ($R^1$=cyano). Redn. of the latter and subsequent diazotization-hydroxylation and chlorination gave III ($R^1$ = $ClCH_2$), which underwent BuLi induced substitution reaction with $AcNMe_2$ to give III ($R^1$ = Ac). Polyphosphoric acid catalyzed cyclization of III ($R^1$= Ac) gave I (R = 4-Me).
Thiophene-13: Citing 1.

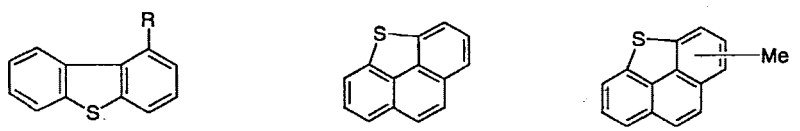



146) **Synthesis of 2-substituted 3-(2-benzo[*b*]thienyl)- or 3-(2-thienyl)-3-(methylthio)acrylonitriles.** Fukuda, Shinichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1983), **20**(9), 1793-6. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 100:85530 AN 1984:85530 CAPLUS. **Abstract**---Dithio ester I was converted to acrylonitriles II (R = cyano, $CO_2Me$, $CONH_2$). I was treated with NaH, $CH_2(CN)_2$, and $Me_2SO_4$ in THF to give II (R= cyano). Similarly prepd. was thiophene analog III. 2-Lithiobenzothiophene reacted with $(MeS)_2C{:}C(CN)R$ (R = cyano, $CO_2Me$) to yield the resp. II.
CS-43: KD-53: Citing 2.



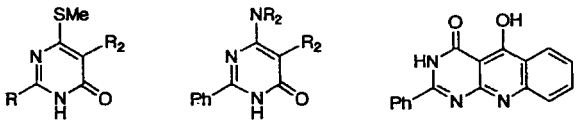

147) **The synthesis of dinaphthothiophenes.** Tedjamulia, Marvin L.; Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1983), **20**(5), 1143-8. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 100:22534 AN 1984:22534 CAPLUS. **Abstract**---Dinaphtho[1,2-*b*:2',3'-*d*]thiophene, dinaphtho[2,1-*b*;2',3'-*d*]thiophene, dinaphtho-[1,2-*b*:1',2'-*d*]thiophene, dinaphtho[2,1-*b*; 1',2'-*d*]thiophene and dinaphtho[1,2-*b*:2',1'-d]thiophene were prepd.
Thiophene-12: Citing 14.

148) **The synthesis of phenanthro[4,5-bcd]thiophene and the four monomethylphenanthro[4,5-*bcd*]-thiophenes.** Tedjamulia, Marvin L.; Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1983), **20**(5), 1149-52. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 100:6241 AN 1984:6241 CAPLUS. **Abstract**---The title thiophenes I (R = 1-, 2-, 3-Me) were prepd. from the dibenzothiophenes II (R = 6-, 7-, 8-Me, $R^1$ = $CH_2Cl$) via cyclization of II ($R^1$ = $CH_2CHO$). I (R = 8-Me) was similarly prepd. via cyclization of II (R = H, $R^1$ = $CH_2COMe$).
Thiophene-11: Citing 3.

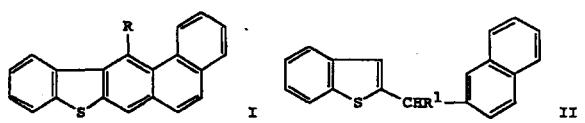



149) **Reaction of ketenethioacetals with carboxamides.** Kohra, Shinya; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1983), **20**(9), 1745-50. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 99:194921AN 1983:594921 CAPLUS. **Abstract**---$(MeS)_2C{:}C(CN)CO_2Me$ reacted with $RCONH_2$ [I; R = Me, $ClCH_2$, Ph,

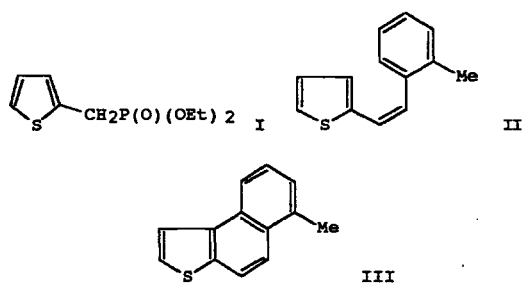
4-$R^1C_6H_4$, $PhCH{:}CH_2$ ($R^1$ = Me, OMe, Cl, $NO_2$)] in the presence of NaH to give $RCONHC(SMe){:}C(CN)CO_2Me$ (II), which cyclized on refluxing in MeOH to give III ($R^2$ = $CO_2Me$). $(MeS)_2C{:}C(CN)_2$ underwent direct cyclocondensed with I to give III ($R^2$ = CN). II (R = Ph) underwent cyclocondensed with $HNR^3R4$ ($R^3$ = H, $R^4$ = Ph, $PhCH_2$, cyclohexyl; $NR^3R^4$ = morpholino) to give IV. IV ($R^3$ = H, $R^4$ = Ph) cyclyzed in refluxing $Ph_2O$ to give V.
KD-52: Citing 4.




150) **The synthesis of benzo[*b*]phenanthro[*d*]thiophenes and anthra[*b*]benzo[*d*]thiophenes.** Tedjamulia, Marvin L.; Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1983), 20(4), 861-6. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 99:175517 AN 1983:575517 CAPLUS. **Abstract**---All isomers of the unsubstituted title ring systems [e.g., benzo[*b*]phenanthro[3,2-*d*]thiophene (I; R = H)] together with I (R = Me) were prepd. Thus, benzo[*b*]thiophene was lithiated with BuLi and treated with 2-naphthaldehyde to give II ($R^1$ = HO), which was reduced by $LiAlH_4$-$AlCl_3$ to give II ($R^1$ = H). Treating the latter with $Cl_2CHOMe$ in the presence of $SnCl_4$ gave I (R = H).
Thiophene-10: Citing 7.

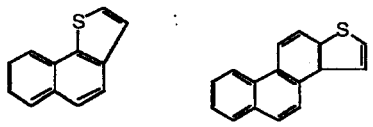



151) **Synthesis of all of the monomethyl isomers of naphtho[2,1-*b*]thiophene.** Tominaga, Yoshinori; Tedjamulia, Marvin L.; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1983), 20(2), 487-90. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 99:53519 AN 1983:453519 CAPLUS. **Abstract**---All isomers of the monomethylnaphtho[2,1-*b*]thiophenes were synthesized by photocyclization of 2-styrylthiophenes which were either prepd. by the Wadsworth-Emmons reaction or by the condensation of 2-lithiothiophene with carbonyl compds. Thus, NaH catalyzed condensation of 2-$MeC_6H_4CHO$ with the phosphonate I gave the methylstyrylthiophene II. Photolysis of II in $C_6H_6$ contg. iodine gave the methylnaphthothiophene III.
Thiophene- 9: Citing 6.

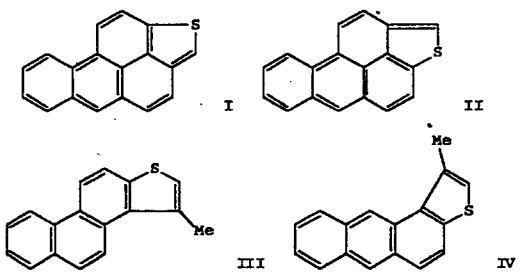



152) **Microbial mutagenicity of 3- and 4-ring polycyclic aromatic sulfur heterocycles.** Pelroy, Richard A.; Stewart, Dorothy L.; Tominaga, Yoshinori; Iwao, Masatomo; Castle, Raymond N.; Lee, Milton L. Biol. Dep., Battelle Mem. Inst., Richland, WA, USA. *Mutation Research* (1983), 117(1-2), 31-40. CODEN: MUREAV ISSN: 0027-5107. Journal written in English. CAN 98:193145 AN 1983:193145 CAPLUS. **Abstract**---The stable isomers of 3- and 4-ring polycyclic arom. S heterocycles were tested for mutagenicity in the Ames std. plate incorporation test and a liq. pre-incubation modification of the Ames test. Of the 4 3-ring compds. tested, only naphtho[1,2-*b*]thiophene (I) [234-41-3] was mutagenic. Of the 4-ring compds., 7 of 13 were mutagenic in the std. Ames or pre-incubation Ames test. The highest activity for the 4-ring compds. was obsd. for phenanthrol[3,4-*b*]thiophene [195-52-8], a compd. of approx. the same mutagenic potency in the Ames test as benzo[*a*]pyrene [50-32-8]. The other active 4-ring compds. were of

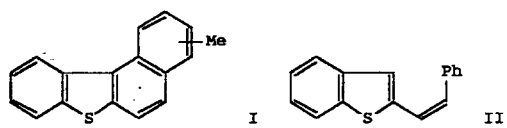
considerable less mutagenic potency than phenanthrol[3,4-*b*]thiophene. Mutagenicity for 2 of the 4-ring arom. thiophenes could only be detected in the liq. pre-incubation Ames test. Salmonella typhimurium TA 100 was the most sensitive strain to mutagenesis by these compds., followed by TA 98. All mutagenesis was indirect, requiring metabolic activation.
Thiophene-8: Citing 28.



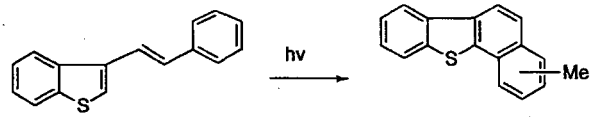
153) **Synthesis of benzo[4,5]phenaleno[1,9-*bc*]thiophene and benzo[4,5]phenaleno[9,1-*bc*]thiophene.** Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1982), **19**(5), 1125-30. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 98:89105 AN 1983:89105 CAPLUS. **Abstract**---Two pentacyclic thiophenes, I and II were synthesized via the corresponding methylphenanthrothiophene (III, IV).
Thiophene-7: Citing 1.



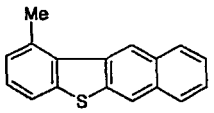
154) **The synthesis of all of the monomethyl isomers of benzo[*b*]naphtho[1,2-*d*]thiophene.** Tominaga, Yoshinori; Pratap, Ram; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1982), **19**(4), 871-7. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 98:53579 AN 1983:53579 CAPLUS. **Abstract**---All 10 isomers of monomethylbenzonaphthothiophene I were synthesized by photocyclization of Me derivs. of styrylbenzo[*b*]thiophene II which were prepd. by the Wadsworth-Emmons reaction or the Wittig reaction.
Thiophene-6: Citing 6.



155) **The synthesis of the monomethyl isomers of benzo[*b*]naphtho[2,1-*d*]thiophene.** Tominaga, Yoshinori; Pratap, Ram; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1982), **19**(4), 859-63. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 98:4452 AN 1983:4452 CAPLUS. **Abstract**---All isomers of the monomethylbenzo[*b*]naphtho[2,1-*d*]thiophenes (I) were prepd. by photocyclization of 3-styrylbenzo[*b*]thiophenes. The 1-, 3-, 4-, and 5-methylbenzo[*b*]naphtho[2,1-*d*]thiophenes were prepd. by irradn. of the corresponding methylated 3-styrylbenzo[*b*]thiophenes which were prepd. by the Wadsworth-Emmons reaction of di-Et benzo[b]thenylphosphonate with tolualdehydes and PhCOMe. The 7-, 8-, 9- and 10-methylbenzo-[*b*]naphtho[2,1-*d*]thiophenes were synthesized by decarboxylation of 7-, 8-, 9- and 10-methylbenzo-[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic acid with Cu in quinoline. These carboxylic acids were prepd. by photocyclization of the corresponding 2-(benzo[*b*]thiophen-3-yl)-3-phenylpropenoic acids which were prepd. by the condensation of the methylated benzo[*b*]thiophene-3-ylacetic acids with PhCHO in the presence of $Et_3N$-$Ac_2O$.
Thiophene-5: Citing 2.

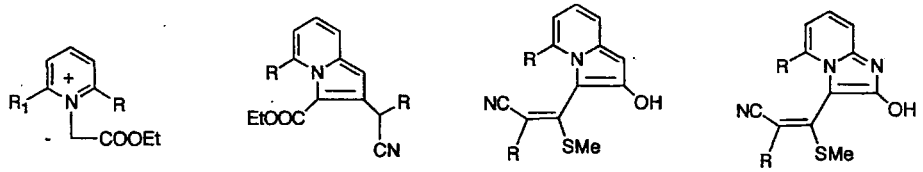



156) **The synthesis of the monomethyl derivatives of benzo[*b*]naphtho[2,3-*d*]thiophene.** Pratap, Ram; Tominaga, Yoshinori; Castle, Raymond N.; Lee, Milton L. Dep. Chem., Univ. South Florida, Tampa, FL, USA. *Journal of Heterocyclic Chemistry* (1982), **19**(4), 865-9. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 97:215920 AN 1982:615920 CAPLUS. **Abstract**---All the title isomers were prepd. by a variety of methods. Thus, *p*-$MeC_6H_4SH$ was treated with 3-bromo-2-decalone followed by cyclization and dehydrogenation to give the 2-Me deriv. I.
Thiophene-4: Citing 1.

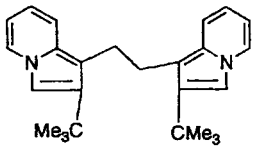


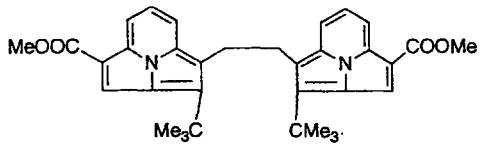

157) **Mesogenic polysiloxane stationary phase for high-resolution gas chromatography of isomeric polycyclic aromatic compounds.** Kong, Robert C.; Lee, Milton L.; Tominaga, Yoshinori; Pratap, Ram; Iwao, Masatomo; Castle, Raymond N. Dep. Chem., Brigham Young Univ., Provo, UT, USA. *Analytical Chemistry* (1982), **54**(11), 1802-6. CODEN: ANCHAM ISSN: 0003-2700. Journal written in English. CAN 97:79432 AN 1982:479432 CAPLUS. **Abstract**---The open tubular column gas chromatog. properties of a new mesogenic polysiloxane phase are described and compared with those of a poly(methylphenylsiloxane) (SE-52). The former is shown to yield high column efficiency commensurate with its gumlike character, yet concomitant high selectivity for isomers of polycyclic arom. hydrocarbons and sulfur heterocycles. The nematic temp. range of the new phase, 70-300° C, exceeds by several factors those of previously described liq. crystal stationary phases.
Citing 9.

158) **Synthesis of indolizine derivatives and their reactions. V.** Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1981), **101**(11), 980-90. CODEN: YKKZAJ ISSN: 0372-7750. Journal written in Japanese. CAN 96:217667 AN 1982:217667 CAPLUS. **Abstract**---2,6-Dimethyl-1-ethoxycarbonylmethylpyridinium bromide (I, R = $R^1$ = Me) reacted with $(MeS)_2C{:}CR^2CN$ ($R^2$ = CN, $CO_2Et$) in the presence of $K_2CO_3$ to afford 3-ethoxycarbonylindolizines II and 3-vinylindolizines III. I (R = $NH_2$, $R^1$ = Me, H) reacted with $(MeS)_2C{:}CR^2CN$ ($R^2$ = CN, $CO_2Et$) in the presence of $K_2CO_3$ only to give 3-vinylimidazo[1,2-*a*]pyridine derivs. e.g. IV. I (R = $R^1$ = Me) was treated with NaH, $CS_2$ and then Me2SO4 to afford Me 2-hydroxy-5-methylindolizine-3-dithiocarboxylate. Imidazo[1,2-*a*]pyridine-3-dithiocarboxylate derivs. were obtained from I (R = $NH_2$, $R^1$ = Me, H). Some reactivities of the dithiocarboxylates with amines or active methylene compd. were described.
KD-51: Citing 3.

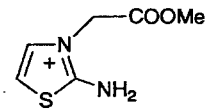



159) **Studies on indolizine derivatives. VI. Synthesis of cycl[3.2.2]azinophane derivative.** Goto, Hiroshi; Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1982), **17**(Spec. Issue), 325-9. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 96:142825 AN 1982:142825 CAPLUS. **Abstract**---Bisindolizine deriv. I was obtained by the reaction of 1,4-di(2-pyridyl)butane with $BrCH_2COCMe_3$. Cycloaddn. reaction of I with Me propiolate afforded biscyclo[3.2.2]azine deriv. II, which was reduced by $LiAlH_4$, followed by dehydration to give the unstable [2.2.2.2](1,4)cycl[3.2.2]azinophane III.
Citing 0.

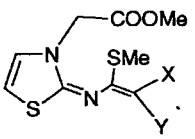


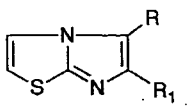

160) **Synthesis of imidazo[2,1-*b*]thiazole derivatives.** Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1981), **101**(11), 991-6. CODEN: YKKZAJ ISSN: 0372-7750. Journal written in Japanese. CAN 96:104144 AN 1982:104144 CAPLUS. **Abstract**---Aminothiazolium deriv. I reacted with ketene thioacetals, e.g., $(MeS)_2C{:}C(CN)_2$, in the presence NaH or Et3N to afford iminodihydrothiazoles, e.g., II [Z = $(NC)_2C$, $MeO_2CC(CN)$, tosylimino]. Treating II with NaOMe resulted in cyclization to give imidazo[2,1-*b*]thiazoles III [R = $CO_2Me$, $R^1$ = $CH(CN)_2$, $CH_2CN$; R = H, $R^1$ = tosylamino].
KD-50: Citing 1.




I

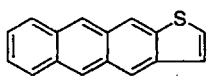



II




III

161) **Synthesis of anthra[b]thiophenes and benzo[*b*]naphtho[*d*]thiophenes.** Tominaga, Yoshinori; Lee, Milton L.; Castle, Raymond N. Dep. Chem., Brigham Young Univ., Provo, UT, USA. *Journal of Heterocyclic Chemistry* (1981), **18**(5), 967-72. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 96:6503 AN 1982:6503 CAPLUS. **Abstract**---All isomers of the parent anthra[*b*]thiophenes and benzo[*b*]naphthol[*d*]thiophenes, e.g. I, II, III, IV, V, and VI were synthesized by, e.g., cyclocondensation or photocyclization.
Thiophene-3: Citing 12.

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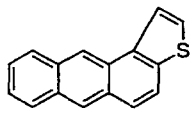


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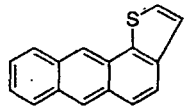
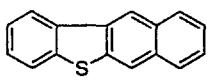
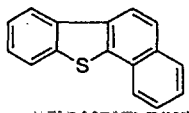


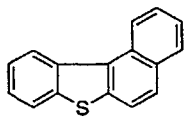

III




IV

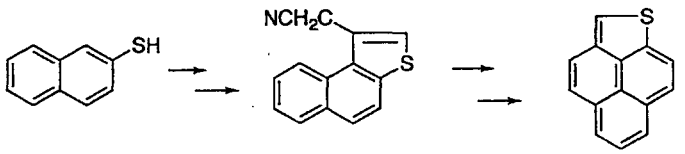



V



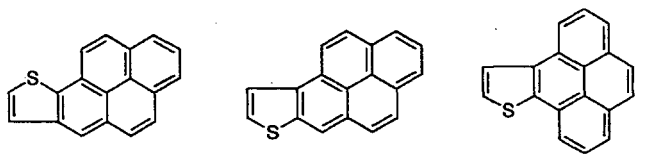

VI

162) **Synthesis of phenaleno[1,9-*bc*]thiophene.** Tominaga, Yoshinori; Lee, Milton L.; Castle, Raymond N. Dep. Chem., Brigham Young Univ., Provo, UT, USA. *Journal of Heterocyclic Chemistry* (1981), **18**(5), 977-9. CODEN: JHTCAD ISSN: 0022-152X. *Journal written in English.* CAN 95:219933 AN 1981:619933 CAPLUS. **Abstract**---Cyclization of 2-acetonylthionaphthalene, prepd. from 2-mercaptonaphthalene (I) and chloroacetone, by polyphosphoric acid gave 1-methylnaphtho[2,1-*b*]thiophene (II) in 64% overall yield from I. By bromination with *N*-bromosuccinimide, II was converted in 40% yield into 1-bromomethylnaphtho[2,1-*b*]thiophene (III), which was treated with KCN in a phase-transfer medium to give 1-cyanomethylnaphtho[2,1-*b*]thiophene (IV) in good yield. IV was reduced to the corresponding aldehyde and then cyclized with polyphosphoric acid to phenaleno[1,9-*bc*]thiophene (V) in 24% overall yield from IV.
Thiophene-2: Citing 6.

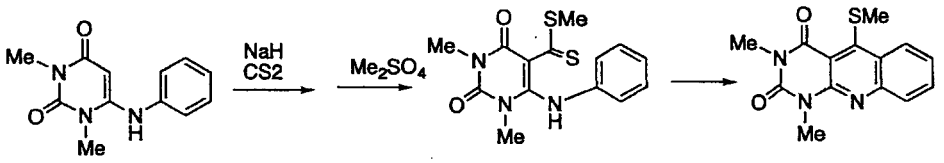



163) **Synthesis of pyreno[*b*]thiophenes.** Pratap, Ram; Tominaga, Yoshinori; Lee, Milton L.; Castle,

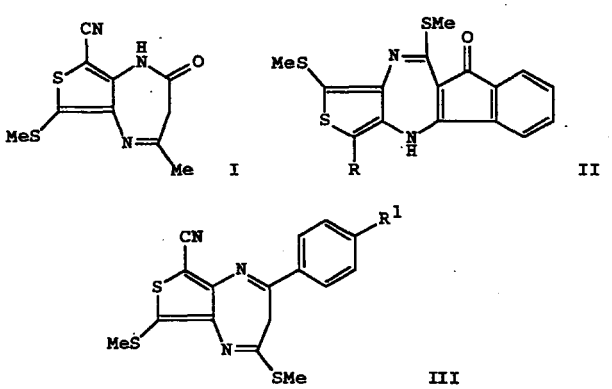
Raymond N. Dep. Chem., Brigham Young Univ., Provo, UT, USA. *Journal of Heterocyclic Chemistry* (1981), **18**(5), 973-5. CODEN: JHTCAD ISSN: 0022-152X. Journal written in English. CAN 95:219932 AN 1981:619932 CAPLUS. **Abstract**—The synthesis of all the isomers of pyreno[b]thiophene namely, pyreno[1,2-*b*]thiophene (I), pyreno[2,1-*b*]thiophene (II) and pyreno[4,5-*b*]thiophene (III) is described. Their spectral characteristics are also discussed.
Thiophene-1: Citing 2.



164) **A new synthesis of pyrimido[4,5-*b*]quinoline-2,4-(1*H*,3*H*)-diones by reaction of 6-arylamino-1,3-dimethyluracils with carbon disulfide.** Tominaga, Yoshinori; Okuda, Hiroto; Tochiki, Mutushi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1981), **15**(2), 679-83. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 94:192263 AN 1981:192263 CAPLUS. **Abstract**—The uracils I (R = H, 4-Me, 4-OMe, 3-OMe, 2-OMe, $R^1 = R_2 = H$) cyclized with $CS_2$-NaOH, followed by treatment with $Me_2SO_4$ to give II (R = H, 7-Me, 7-OMe, 8-OMe, 9-OMe, $R^3$ = Me). Treatment of I (R-$R^2$ = H) with $CS_2$-$Me_2SO_4$, followed by NaOH, gave I (R = $R^2$ = H, $R^1$ = $CS_2Me$; R = $R^1$ = H, $R^2$ = $CS_2Me$). The latter compd. was cyclized by heating to II (R = $R^3$ = H) which was methylated with $Me_2SO_4$-NaOH to II (R = H, $R^3$ = Me). II (R = $R^3$ = H) and III were also obtained by treating I (R-$R^2$ = H) with $CS_2$-NaOH, followed by HCl. II were dethiolated with Raney Ni or were converted to their hydroxy analogs with $H_2O_2$.
CS-41: Citing 2.

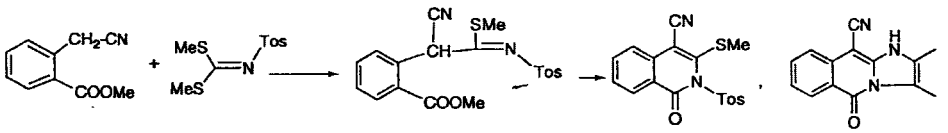



165) **Synthesis of thieno[3,4-*b*][1,4]diazepine derivatives.** Tominaga, Yoshinori; Fujito, Hiroshi; Norisue, Hajime; Ushirogochi, Atsuyuki; Matsuda, Yoshiro; Kobayashi, Goro. Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1980), **100**(7), 699-705. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 94:47285 AN 1981:47285 CAPLUS. **Abstract**—The reaction of 5-substituted 3,4-diamino-2-(methylthio)thiophenes with 1,3-dicarbonyl compds. (Me acetoacetate, di-Et or di-Me acetonedicarboxylate, diketene, Et benzoylacetate) gave the corresponding thienodiazepine derivs., e.g. I. The condensation of the substituted 3,4-diamino-2-(methylthio)thiophenes with ketene thioacetal derivs. 2-bis(methylthio)-methylene-1,3-indandione, 3,3-bis(methylthio)-1-(*p*-substituted phenyl)-2-propen-1-one afforded the corresponding indenodiazepinothiophenones II (R = cyano, $CO_2Et$) and thienodiazepines III ($R^1$ = H, Cl, Br) in good yields.
CS-40: KD-49: Citing 1.

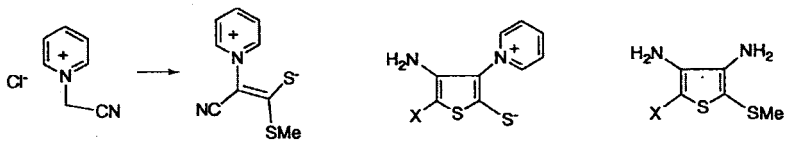



166) **Sulfonyl ketene thioacetal. IV. Syntheses of isoquinoline derivatives using *N*-bis(methylthio)-methylene-*p*-tolylsulfonamide.** Tominaga, Yoshinori; Hidaki, Shozo; Matsuda, Yoshiro; Kobayashi,

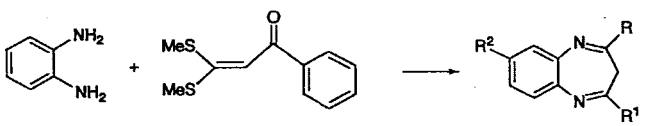
Goro; Sakemi, Kanro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1980), **100**(4), 456-9. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 93:239176 AN 1980:639176 CAPLUS. **Abstract**---Treatment of o-$MeO_2CC_6H_4C(CN)$:$C(SMe)NHSO_2C_6H_4Me$-p (I), prepd. from $(MeS)_2C$:$NSO_2C_6H_4Me$-p and o-$MeO_2CC_6H_4CH_2CN$, in the presence of NaH with HCl yielded the isoquinolinone II. Similarly, the reaction of o-$MeO_2CC_6H_4CH_2CN$ with $(MeS)_2C$:NCN gave 24% of 2,4-dicyano-1,2-dihydro-3-methylthioisoquinolin-1-one. I reacted with $HOCH_2CH_2NH_2$, $PhCH_2NH_2$, and $H_2NNH_2 \cdot H_2O$ to give the corresponding 3-amino-4-cyano-1,2-dihydroisoquinolin-1-ones and the pyrazolo-isoquinolin-5-one III. Reaction of I with o-$(H_2N)_2C_6H_4$ and $H_2NCH_2CH_2NH_2$ the benzimidazoiso-quinolinone IV (89%) and 76% imidazo[1,2-*b*]isoquinolin-5(5*H*)-one.
KD-48: Citing 1.



167) **Synthesis and reaction of 3,4-diaminothiophenes.** Tominaga, Yoshinori; Fujito, Hiroshi; Norisue, Hajime; Ushirogochi, Atsuyuki; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1979), **99**(11), 1081-90. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 93:46286 AN 1980:446286 CAPLUS. **Abstract**---Addn. of pyridinium chloride I and $CS_2$ gave Ia, which was alkylated by $XCH_2Y$ (X = Cl, Br; Y = CN, $CO_2Et$, Bz, $CONH_2$), cyclized, and iodomethylated to give II ($R^1$ = CN, $CO_2Et$, Bz, $CONH_2$; $R^2$ = pyridinio iodide). Cleavage of II iodide by addn. of $MeNH_2$ followed by cyclization, acid hydrolysis, and neutralization gave II (R1 = CN, $CO_2Et$, Bz, $CONH_2$; $R^2$ = $NH_2$). Also prepd. were thieno[3,2-*d*]pyrimidinones III ($R^3$ = Me, Ph; $R^4$ = $NH_2$, NHBz, pyridinio chloride) and the thieno[3',4':4,5]imidazo[1,2-*a*]pyridine IV.
CS-39: Citing 1.

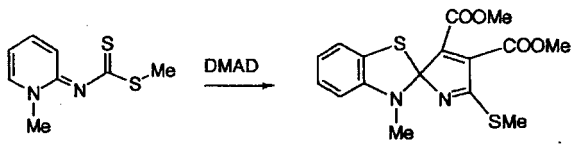


168) **Synthesis of 1,5-benzodiazepines.** Ushirogochi, Atsuyuki; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1980), *14*(1), 7-10. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 93:8143 AN 1980:408143 CAPLUS. **Abstract**---Benzodiazepines I (R = SMe; $R^1$ = Ph, 4-$ClC_6H_4$, 4-$BrC_6H_4$, 2-thienyl; $R^2$ = $NO_2$, Cl) were prepd. in 55-97% yield by condensing 3,4-$(H_2N)_2C_6H_3R^2$ with $(MeS)_2C$:$CHCOR^1$. I (R = $NHCH_2Ph$, morpholino, 4-methylpiperazino; $R^1$ = 4-$ClC_6H_4$; $R^2$ = $NO_2$) were obtained in 43-90% yield by treating I (R = SMe, $R^1$ = 4-$ClC_6H_4$, $R^2$ = $NO_2$) with amines. I (R = SMe; $R^1$ = Ph, 4-$ClC_6H_4$; $R^2$ = $NO_2$) were oxidized to the ketones by $H_2O_2$.
KD-47: Citing 2.

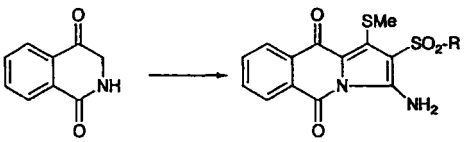


169) **Synthesis and reactions of heterocyclic dithiocarbamates.** Mizuyama, Kazumichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Kao Soap, Co., Ltd., Tokyo, Japan. *Chemical & Pharmaceutical Bulletin* (1979), **27**(12), 2879-89. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 93:7964 AN 1980:407964 CAPLUS. **Abstract**----[(Alkylthio)thiocarbonyl- imino]pyridines I (R = Me, $PhCH_2$; $R^1$, $R^2$, $R^3$ = H, Me) were prepd. by reaction of 2-amino-1-methyl- pyridinium iodides with $CS_2$ in the presence of NaH and subsequent methylation with $Me_2SO_4$. Similarly, 1-methyl-4-[(methylthio)thiocarbonylimino]-1,4-dihydropyridine (II), 1-methyl-2-[(methylthio)thio-carbonylimino]-1,2-dihydrothiazole, and 1-methyl-2-[(methylthio)thiocarbonylimino]-1,2-dihydrobenzo-thiazole (III) were prepd. by reaction of the corresponding 2-imino- and 4-imino-N-Me heterocyclic compds. with $CS_2$. Reaction of I with $MeO_2CC.tplbond.CCO_2Me$ gave dihydropyridines IV. Reaction of II with $MeO_2CC.tplbond.CCO_2Me$ (2 mol) gave cyclobutaazocine (V). Reaction of III with $MeO_2CC.tpl$-

bond.$CCO_2Me$ yielded spirobenzothiazole VI. 2-[[Bis(methylthio)methylene]amino]-1-methyl- pyridinium iodide and 2-[[bis(methylthio)methylene]amino]-1-methylbenzothiazolium iodide reacted with nucleophiles to yield products resulting from substitution of one or two methylthio groups.
CS-38: Citing 4.

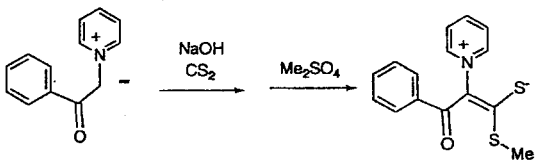



170) **Sulfonyl ketenethioacetal. III. Reaction of sulfonyl ketenethioacetal with active methylene compounds.** Hidaki, Shozo; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro; Sakemi, Kanro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1979), **99**(12), 1234-9. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 92:198238 AN 1980:198238 CAPLUS. **Abstract**---Ketene thioacetals $(MeS)_2C{:}CR^1SO_2R$ (I; R = Ph, p-$MeC_6H_4$; $R^1$ = COMe, CN, CO2Et) were condensed with active methylene compds. and K2CO3 in DMF. Thus, I (R = Ph, $R^1$ = COMe) was treated with $CH_2(CN)_2$ to give 38% 5-phenylsulfonyl-3-cyano-6-methyl-4-methylthio-2-pyridone. The condensation of I (R = *p*-$MeC_6H_4$, $R^1$ = CN) with $MeNO_2$ gave 48% 2-hydroxyimino-3-methylthio-5-oxo-4-*p*-tolylsulfonylpyrroline. Reactions of I (R = Me, Ph; $R^1$ = CN) with 1,4-dioxo-1,2,3,4-tetrahydroisoquinoline and 2,3-dihydrobenzo[*b*]thiophen-3-one gave 30% pyrroloisoquinolines (II) and 67-82% pyridobenzothiophenes (III), resp.
CS-37: Citing 3.

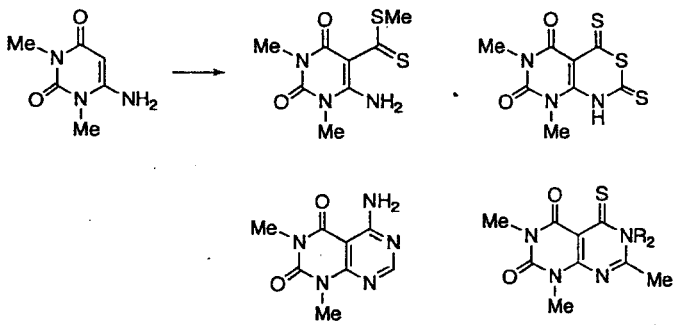



171) **Enamino carbodithioates. III. Methyl 6-aminouracil-5-carbodithioates. 3. Synthesis and reactions of 3-methylthioisothiazolo[3,4-*d*]pyrimidine-4,6(5*H*,7*H*)-diones.** Okuda, Hiroto; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1979), **99**(10), 989-92. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 92:128845 AN 1980:128845 CAPLUS. **Abstract**----3-Methylthioiso-thiazolopyrimidinediones I (R = Me, Ph) were prepd. by treatment with Me 6-aminouracil-5-carbodithioates, prepd. by the reaction of 6-aminouracil with $CS_2$ and $Me_2SO_4$ in the presence of alkali, with iodine in $Me_2SO$ in a good yield. The reaction of I with amines, amides, and active methylene compds. gave the corresponding substituted products.
CS-36: Citing 1.

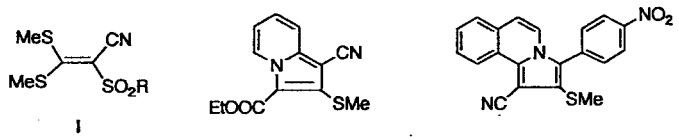

172) **1-(1-Pyridinio)-1-benzoyl-2-methylthio-2-thioxo-1-ethanide.** Tominaga, Yoshinori; Kobayashi, Goro; Tamura, Chihiro; Sato, Sadao; Hata, Tadashi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry* (1979), **B35**(10), 2443-5. CODEN: ACBCAR ISSN: 0567-7408. Journal written in English. CAN 91:202599 AN 1979:602599 CAPLUS. **Abstract**---The title compd., $C_{15}H_{13}NOS_2$, is monoclinic, space group P21/c, with a 9.533(2), b 13.710(2), c 119284(2) .ANG., and β 106.6(3)°; Z = 4. The structure was refined by full-matrix least-squares to a final R = 0.054. The pyridinium betaine N+-C(5) length is 1.470 .ANG.. The intramol. S-...N+ distance is 2.937 .ANG.
CS-35: Citing 2.




173) **Enamino carbodithioates. I. Methyl 6-aminouracil-5-carbodithioates. 1. Synthesis and reactions.** Tominaga, Yoshinori; Machida, Tsuyoshi; Okuda, Hiroto; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1979), **99**(5), 515-20. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 91:175307 AN 1979:575307 CAPLUS. **Abstract**---The 6-aminouracils I (R = Me, Ph, $R^1$ = H) treated with $CS_2$ and $Me_2SO_4$ in NaOH-DMSO gave dithiocarboxylates I (R = MePh; R1 = $CS_2Me$). An excess of $CS_2$ in the previous reaction with I (R = Me, $R^1$ = H) gave the pyrimido[4,5-*d*][1,3]thiazine II in good yield. The reaction of I (R = Me, Ph; $R^1$ = $CS_2Me$) and $R^2_2NH$ ($R^2$ = H, $NH_2$, Me, $PhCH_2$, cyclohexyl, morpholino, $HOCH_2CH_2$, $(EtO)_2CHCH_2$), yielded thiocarbamoyluracils I [R = Me, Ph, $R^1$ = $C(S)NR^2_2$] in 31-91% yields. I [R = Me, $R^1$ = C(S)SMe] and $HCONH_2$ reacted to yield III. Also prepd. were pyrimido[4,5-*d*]pyrimidines IV ($R^2$ = H, Me; X = S) and IV ($R^2$ = $PhCH_2$, X = O) from the reaction of I [R = Me, $R^1$ = $C(S)NR^2_2$, $R^2$ = H, Me, $PhCH_2$] with $Ac_2O$.
CS-34: Citing 1.

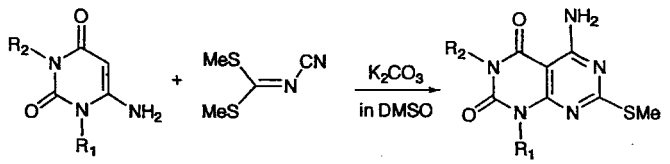



174) **Sulfonyl ketene thioacetal. II. Reactions of pyridinium and isoquinolinium *N*-ylides with phenylsulfonyl ketenethioacetal.** Tominaga, Yoshinori; Hidaki, Shozo; Matsuda, Yoshiro; Kobayashi, Goro; Sakemi, Kanro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1979), **99**(5), 540-2. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 91:157559 AN 1979:557559 CAPLUS. **Abstract**---Treatment of $PhSO_2CH_2CN$ with NaH in THF and then with $CS_2$ and $Me_2SO_4$ gave 75% sulfonyl ketene thioacetal I, which cyclized with the pyridinium halides II (R = $CO_2Et$, CN, 4-$O_2NC_6H_4$; $R^1$, $R^2$ = H, Me; X = Br, Cl) in refluxing EtOH contg. $Et_3N$ to give the indolizines III in 38-92% yields. Similarly, 2-(4-nitrobenzyl)isoquinolinium chloride and I gave 85% pyrroloisoquinoline IV.
KD-46: Citing 4.

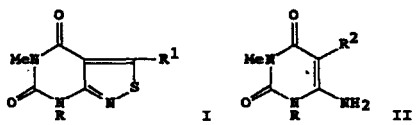



I

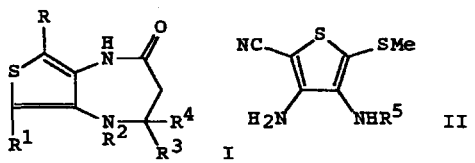
175) **Synthesis of pyrimido[4,5-*d*]pyrimidines.** Tominaga, Yoshinori; Okuda, Hiroto; Mitsutomi, Yoshiro; Matsuda, Yoshiro; Kobayashi, Goro; Sakemi, Kanro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1979), **12**(4), 503-4. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 91:5192 AN 1979:405192 CAPLUS. **Abstract**---Reaction of aminouracil I ($R^1$ = $R^2$ = Me; $R^1$ = Ph, $R^2$ = H, Me) with $(MeS)_2C$:NCN in DMF contg. $K_2CO_3$ gave 38-72% II. Redn. of II ($R^1$ = $R^2$ = Me) with Raney Ni gave III.
KD-45: Citing 4.



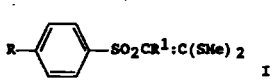
176) **Enamino dithiocarboxylates. II. Methyl 6-aminouracil-5-dithiocarboxylates. 2. Synthesis and reactions of 3-methylthioisothiazolo[3,4-*d*]pyrimidine-4,6(5*H*,7*H*)-diones.** Okuda, Hiroto; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1979), **12**(4), 485-8. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 91:5191 AN 1979:405191 CAPLUS. **Abstract**---Isothiazolopyrimidinediones I (R = Me, Ph; $R^1$ = SMe) were obtained by treating uracils II ($R^2$ = H) with $CS_2$ and $Me_2SO_4$ and cyclizing II ($R^2$ = $CS_2Me$) with iodine. I ($R^1$ = SMe) underwent nucleophilic substitution to give I [$R^1$ = amino, $CH(CN)CO_2Me$, $CH(CN)SO_2Ph$].
CS-33: Citing 4.



177) **Synthesis of thieno[3,4-*b*][1,4]diazepin-2-one.** Tominaga, Yoshinori; Fujito, Hiroshi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1979), **12**(3), 401-4. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 90:186910 AN 1979:186910 CAPLUS. **Abstract**---Thienodiazepinones I (R = CN, $R^1$ = MeS, $R^2R^3$ = bond, $R^4$ = Me; $R^2$ = H, $R^3R^4$ = $EtO_2CCH$; R = MeS, $R^1$ = CN, $R^2R^3$ = bond, $R^4$ = Me, Ph) were prepd. in 77-97% yield by cyclocondensation of II ($R^5$ = H) with $MeCOCH_2CO_2Et$, $CO(CH_2CO_2Et)_2$, diketene, or $PhCOCH_2CO_2Et$. Two of the intermediates (II; $R^5$ = $CMe{:}CHCO_2Et$, $COCH_2COPh$) were isolated.
CS-32: Citing 0.

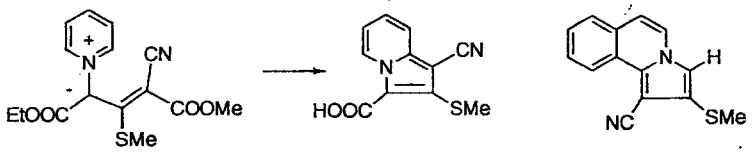


178) **Sulfonyl ketenethioacetals. 1. Synthesis and reaction of sulfonyl ketenethioacetals.** Kashima, Kenichi; Hidaki, Shozo; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro; Sakemi, Kanro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan.*Yakugaku Zasshi* (1979), **99**(1), 38-44. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 90:186863 AN 1979:186863 CAPLUS. **Abstract**---Sulfonyl ketenethioacetal derivs. I (R = H, Me; $R^1$ = Ac, CN) were synthesized by the reaction of sulfonyl carbanions with $CS_2$ in the presence of NaH in THF, followed by treatment with $Me_2SO_4$. The reaction of I with various amines gave the corresponding amine derivs. and heterocyclic compds. (pyrazole, imidazoline, benzimidazoline, oxazoline).
KD-44: Citing 2.

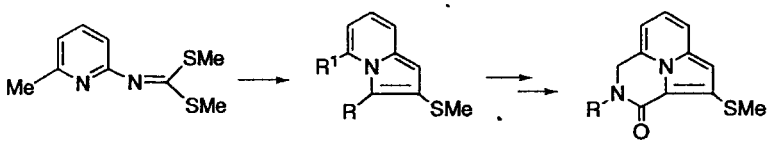


179) **Heterocyclic ketenethioacetal derivatives. XI. Reactions of pyridinium and isoquinolinium allylides.** Fujito, Hiroshi; Tominaga, Yoshinori; Awaya, Hiroshi; Kurata, Keiji; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1978), **98**(10), 1412-16. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 90:72024 AN 1979:72024 CAPLUS. **Abstract**---Desulfurization of pyridinium and isoquinolinium 3-cyano-2-(methylthio)allylides I and II (R = PhCO, $R^1$ = H, $R^2$ = $CO_2Me$, $CO_2Et$; R = $R^2$ = $CO_2Et$, $R^1$ = H) with Raney-Ni gave the corresponding desulfurized allylides. Treating I (R = $R^2$ = $CO^2Et$, $R^1$ = H) and II with 10% NaOH gave indolizine III and pyrrolo[2,1-*a*]isoquinoline IV, resp. Treating I (R = PhCO, $R^1$ = H, $R^2$ = $CO_2Me$; R = PhCO, $R^1$ = Me, $R^2$ =

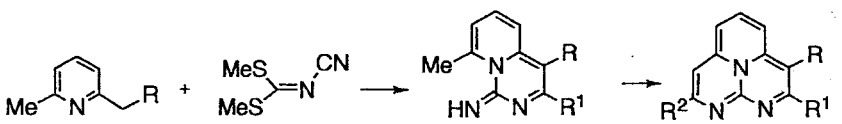
CN) with $H_2NNH_2.H_2O$ gave pyrazoles V ($R^1$ = H, $R^2$ = $CO_2Me$; $R^1$ = Me, $R^2$ = CN) in good yield.
KD-43: Citing 2.



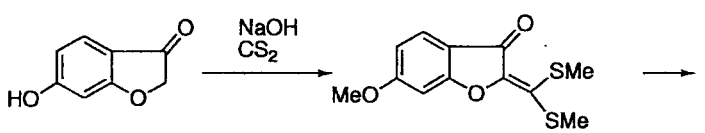
180) **Synthesis of indolizine derivatives and their reactions. II.** Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1978), **98**(5), 631-5. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 90:22892 AN 1979:22892 CAPLUS. **Abstract**---Cyclization of I with $BrCH_2R$ (R = $CO_2Et$, COPh, $CH{:}CHCO_2Et$) at 60° easily gave 1-azaindolizines II ($R^1$ = Me). Oxidn. of II (R = $CO_2Et$; $R^1$ = H, Me) by perphthalic acid gave the 2-methylsulfonyl derivs. Bromination of II (R = $CO_2Et$, $R^1$ = Me) by *N*-bromosuccinimide gave II (R = $CO_2Et$, $R^1$ = $CH_2Br$), cyclization of which with $NH_3$ and $MeNH_2$ gave III ($R^2$ = H and Me, resp.).
KD-42: Citing 6.



181) **Studies on quinolizine derivatives. XVII. Synthesis of diazacycl[3.3.3]azine derivatives. 10.** Kurata, Keiji; Yamada, Miwako; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1978), **98**(5), 623-30. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 89:197443 AN 1978:597443 CAPLUS. **Abstract**---Cyclocondensation of 6-$RCH_2$-substituted 2-methylpyridines (R=CN, $CO_2Me$) with $MeSCR^1{:}NCN$ ($R^1$ = SMe, OEt) gave the resp. 1-imino-8-methyl-1*H*-pyrido[1,2-*c*]pyrimidines, and the latter cyclocondensed with $Ac_2O$ and $EtOCH{:}C(CN)_2$ to give I ($R^2$ = Me) and I (R = H). Decarboxylation of I (R = $CO_2Me$, $R^1$ = MeS, $R^2$ = H) gave I (R = $R^2$ = H, $R^1$ = MeS) (II), which was unstable as the free base. Degrdn. of I (R = $CO_2Me$, $R^1$ = MeS, $R^2$ = Me) gave III as the HBr salt. The NMR data suggested that II may be a 12 π-monocyclic antiaromatic compd.
KD-41: Citing 2.

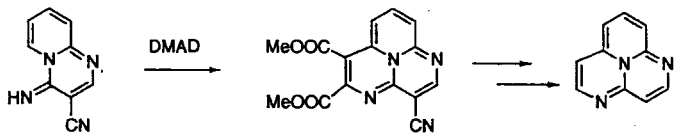


182) **Synthesis and reaction of 2-bis(methylthio)methylenecoumaran-3-ones.** Tominaga, Yoshinori; Kurata, Keiji; Awaya, Hiroshi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1978), *9*(4), 399-404. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 89:42954 AN 1978:442954 CAPLUS. **Abstract**---The coumaranone I, prepd. by reaction of 6-hydroxycoumaran-3-one with $CS_2$ followed by methylation with $Me_2SO_4$, reacted with nucleophiles, e.g., $CH(CO_2Et)_2$, to give the corresponding substitution products of 1 methylthio group in good yield.
CS-31: KD-40: Citing 1.

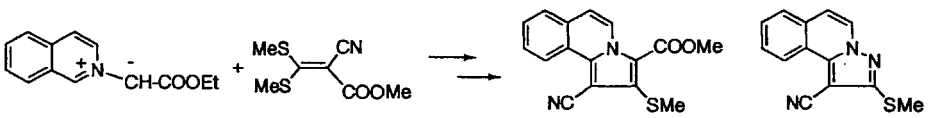


183) **Studies on quinolizine derivatives. XIX. The synthesis of diazacycl[3.3.3]azine derivatives. 13.** Kuya, Mayumi; Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1978), **26**(2),

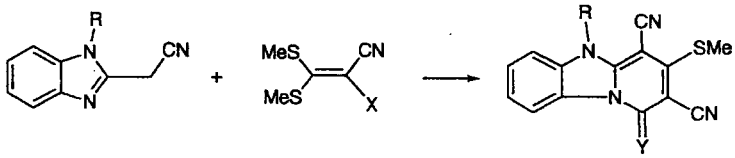
680-1. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 88:190734 AN 1978:190734 CAPLUS. **Abstract**---Reaction of 4-imino-4*H*-pyrido[1,2-*a*]pyrimidine I, and $MeO_2CC.tplbond.CCO_2Me$ or HC.tplbond.$CCO_2Me$, with 5% Pd-C, gave 1,4-diazacycl[3.3.3]azines II (R = $CO_2Me$, H). Moreover, the degrdn. of II (R = H) gave a new parent compd., namely 1,4-diazacycl[3.3.3]azine III, which may be an antiarom. compd. according to the NMR.
Citing 1.



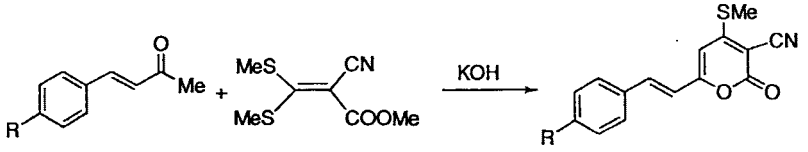

184) **Reaction of isoquinolinium ylides and isoquinolinium imines with ketenethioacetal derivatives.** Fujito, Hiroshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1977), 97(12), 1316-21. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 88:152384 AN 1978:152384 CAPLUS. **Abstract**---Reaction of I (R = $CO_2Et$, $R^1$ = H) (II), $(MeS)_2C:C(CN)_2$ and $NEt_3$ or $K_2CO_3$ in EtOH or DMF gave I [R = $CO_2Et$, $R^1$ = $C(SMe):C(CN)_2$]. Similar reaction of II and $(MeS)_2C:C(CN)CO_2Et$ gave III and that of I (R = $CO_2Me$, $R^1$ = H) and $(MeS)_2C:C(CN)CO_2Me$ gave IV. Reaction of isoquinolinium *N*-imine and $(MeS)_2C:C(CN)CO_2Et$ gave V.
KD-39: Citing 2.



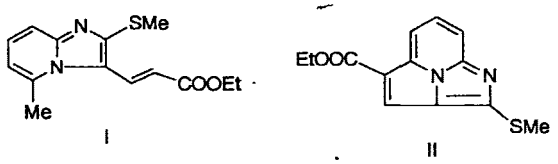

185) **Reactions of benzimidazole derivatives.** Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Bunseki Kiki* (1977), 15(9), 413-19. CODEN: BUKIBO ISSN: 0386-1899. Journal written in Japanese. CAN 88:121047 AN 1978:121047 CAPLUS. **Abstract**---I (R = H, Me) were treated with $CS_2$ and $Me_2SO_4$ to give the 2-C(CN):C(SH)SMe- and 2-:C(CN)C(S)SMe-substituted derivs. Reactions of I (R = H, Me) with $(MeS)_2C:C(CN)CO_2Me$, $(MeS)_2C:C(CN)_2$, and $EtOCH:C(CN)_2$ gave II, III, and IV, resp. I (R = H, Me) and amines ($PhCH_2NH_2$, piperidine, and morpholine) gave the corresponding V ($R^1$ = $PhCH_2NH$, piperidino, morpholino). III and IV were treated with $MeO_2CC.tplbond.CCO_2Me$ to give products such as VI (Z = $NC(CO_2Me):CHCO_2Me$).
KD-38: Citing 4.



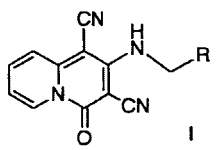

186) **Synthesis of 6-(2-phenylethenyl)-2*H*-pyran-2-one.** Tominaga, Yoshinori; Ushirogochi, Atsuyuki; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1977), 8 193-7. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 88:89471 AN 1978:89471 CAPLUS. **Abstract**---(Methylthio)pyranones I ($R^1$ = H, MeO, Cl) were prepd. by treating $4\text{-}R^1C_6H_4CH:CHCOMe$ with $(MeS)_2C:C(CN)CO_2Me$ in the presence of powd. KOH at room temp. The MeS group of I reacted readily with nucleophiles. Thus, I refluxed in MeOH or Me Cellosolve in the presence of alkali gave alkoxides II ($R^1$ = H, OMe, $R^2$ = Me; $R^1$ = OMe, $R^2$ = $CH_2CH_2OMe$). I with amines in MeOH gave III ($R^1$ = H, MeO, Cl; $NR^3R^4$ = $NHCH_2Ph$, cyclohexylamino, piperidino, morpholino, $NHCH_2CH_2OH$). II and III are dehydrokawain and yangonin derives., resp.
KD-37: Citing 9.



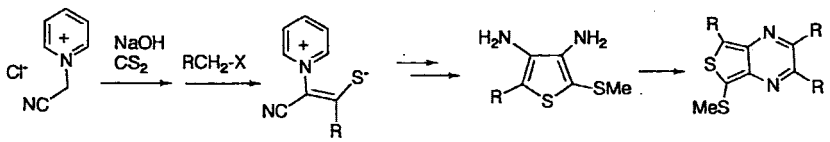
187) **Studies on indolizine derivatives. New synthetic methods for azacycl[3.2.2]azine derivatives. XI.** Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1977), **8**, 293-8. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 88:74340 AN 1978:74340 CAPLUS. **Abstract**---Photolysis of imidazo[1,2-*a*]pyridineacrylate I in EtOH resulted in cyclization to give 40% II. II was also obtained by refluxing I and *N*-bromosuccinimide in $HCCl_3$ in the presence of $Bz_2O_2$.
CS-30: KD-36: Citing 1.



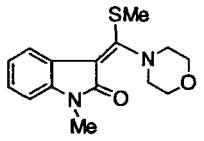
188) **Antitumor activity of heterocyclic and ketenethioacetal derivatives.** Kobayashi, Goro; Matsuda, Yoshiro; Tominaga, Yoshinori; Ohkuma, Mihoko; Shinoda, Hirotaka; Kohno, Morihiro; Mizuno, Den'ichi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1977), 97(9), 1039-45. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 88:44882 AN 1978:44882 CAPLUS. **Abstract**---Eighty-seven compds. of maleimide, five- or six-ring heterocyclic 4*H*-quinolizines, and ethylene derivs. were prepd. and their antitumor activity was examd. using a solid type of Ehrlich carcinoma. 1,3-Dicyano-2-benzylamine-4*H*-quinolizin-4-one (I) [65125-90-8] had some antitumor effect, but no other synthesized compds. were effective.
Citing 3.



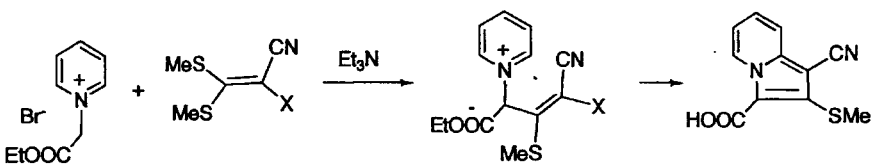
189) **A new synthesis of 3,4-diaminothiophenes.** Tominaga, Yoshinori; Fujito, Hiroshi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1977), 6(11), 1871-6. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 88:37541 AN 1978:37541 CAPLUS. **Abstract**---Thiophenediamines I (R = CN, $CONH_2$, $CO_2Et$, Bz) were prepd. by treating $R^1CH_2CNCl$- ($R^1$ = pyridinio) with $CS_2$-NaOH, treating $R^1C(CN):C(SNa)S$- with $R^2CH_2R$ ($R^2$ = Cl, Br), cyclizing $R^1C(CN):C(S-)SCH_2R$ with $NEt_3$, methylating ylides II ($R^3$ = S-), treating II ($R^3$ = SMe) with $MeNH_2$-HCl and neutralizing. I condensed with $R^4COCOR^4$ ($R^4$ = H, Me, Ph) to give the thienopyrazines III.
CS-29: Citing 0.



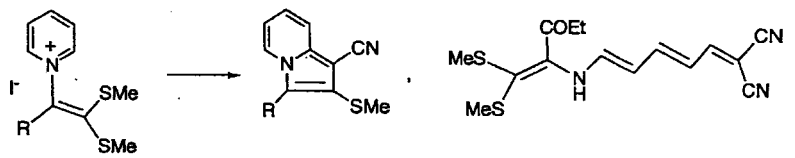
190) **Antitumor activity of indole derivatives.** Kobayashi, Goro; Matsuda, Yoshiro; Tominaga, Yoshinori; Ohkuma, Mihoko; Shinoda, Hirotaka; Kohno, Morihiro; Mizuno, Den'ichi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1977), 97(9), 1033-9. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 88:31980 AN 1978:31980 CAPLUS. **Abstract**---Sixty-one indole derivs. contg. oxindole, spiro-oxindole, and condensed-ring indole were prepd. and their antitumor activity was examd. using a solid type of Ehrlich carcinoma. 1-Methyl-3-(1-methylthio-1-morpholinomethylene)oxindole (I) [15127-79-4] was found to have some antitumor effect, but no other derivs. were found effective.
Citing 8.



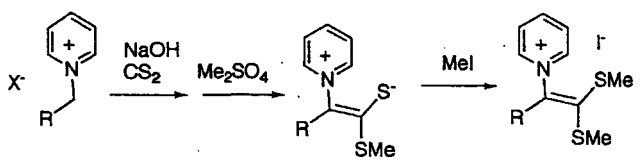
191) **Reaction of pyridinium *N*-ylides with ketene thioacetal derivatives.** Tominaga, Yoshinori; Miyake, Yoshinori; Fujito, Hiroshi; Kurata, Keiji; Awaya, Hiroyoshi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1977), 25(7), 1528-33. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 88:22552 AN 1978:22552 CAPLUS. **Abstract**---Reaction of the pyridinium *N*-ylides with ketenethioacetal in the presence of $Et_3N$ or $K_2CO_3$ as a base in EtOH or DMF gave the pyridinium N-allylides which readily cyclized to give the indolizine derivs. Thus, the pyridinium ylide I and $(MeS)_2C{:}CHNO_2$ gave the indolizine II.
KD-35: Citing 4.



192) **Heterocyclic ketene thioacetal derivatives. IX. Reactions of 1-[2,2-bis(methylthio)vinyl]pyridinium iodides with active methylene compounds.** Tominaga, Yoshinori; Fujito, Hiroshi; Mizuyama, Kazumichi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1977), 25(7), 1519-27. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 88:6669 AN 1978:6669 CAPLUS. **Abstract**---The reaction of 1-[2,2-bis(methylthio)-vinyl]pyridinium iodide derivs. I (R = H, PhCO, $EtO_2C$, $H_2NCO$; $R^1$-$R^3$ = H, Me) with active methylene compds. in the presence of a base in EtOH, DMF, or $Me_2SO$ gave pyridinium allylides, e.g., II, indolizines, e.g., III, and *N*-[2,2-bis(methylthio)vinyl]-*N*-(6,6-disubstituted 1,3,5-hexatrienyl)amine derivs., e.g., $(MeS)_2C{:}CHNHCH{:}CHCH{:}CHCH{:}C(CN)_2$.
KD-34: Citing 3.

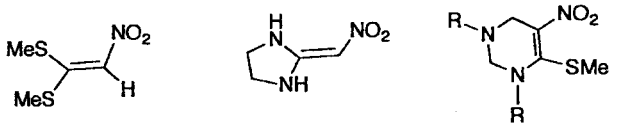


193) **Heterocyclic ketene thioacetal derivatives. VIII. Synthesis of ketene thioacetals having a pyridinium salt.** Tominaga, Yoshinori; Miyake, Yoshinori; Fujito, Hiroshi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1977), *97*(8), 927-32. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 87:201268 AN 1977:601268 CAPLUS. **Abstract**----Ketenethioacetal derivs. I ($R^1$ = Bz, $CO_2Et$, $CONH_2$, CN; $R^2$, $R^3$, $R^4$ = H, Me) were prepd. by alkylation with MeI of II, which were prepd. by the reaction of pyridinium ylides with $CS_2$ in the presence o NaOH.
CS-28: KD-33: Citing 6.

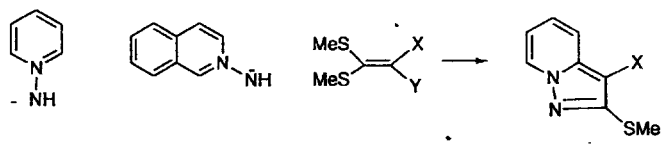


194) **Reaction of 1-nitro-2,2-bis(methylthio)ethylene. V. Reaction with amines.** Sone, Masakatsu; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1977), 97(3), 262-7. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 87:53195 AN 1977:453195 CAPLUS. **Abstract**---$(MeS)_2C{:}CHNO_2$ reacted with $R^1NHR^2$ [$R^1$ = H, $R^2$ = $CH_2Ph$, $CH_2CH(OEt)_2$, Ph; $NR^1R^2$ = piperidino] and $H_2NCH_2CH_2NH_2$ to give

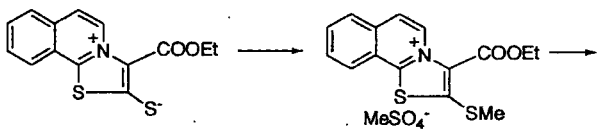
$R^1R^2NC(SMe):CHNO_2$ and $(R^1R^2N)_2C:CHNO_2$ and the imidazolidine I. $PhCH_2NHC(SMe):CHNO_2$ further cyclized with $PhCH_2NH_2$ and HCHO to give the pyrimidine deriv. II.
KD-32: Citing 7.



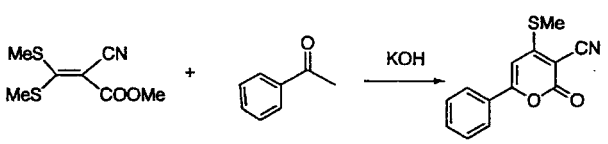
195) **Reaction of pyridinium and isoquinolinium *N*-imines with ketene thioacetals.** Fujito, Hiroshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1977), 6(4), 379-82. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 87:53048 AN 1977:453048 CAPLUS. **Abstract**---Treatment of the isoquinolinium imine I (R = H) with $(MeS)_2C:C(CN)_2$, $(MeS)_2C:CHNO_2$, and $(MeS)_2C:C(CN)CO_2Me$ gave I [R = $C(SMe):C(CN)_2$], pyrrazoloisoquinoline II ($R^1 = NO_2$), and II ($R^1$ = CN), resp. The pyridinium imines III ($R^2$ = H, Me) and pyrazolopyridines IV were prepd. similarly.
KD-31: Citing 3.



196) **Reaction of 3-ethoxycarbonyl-2-methylthiothiazolo[2,3-*a*]isoquinolinium sulfate with active methyl and methylene compounds.** Mizuyama, Kazumichi; Matsuo, Yoko; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1976), 24(6), 1299-304. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 86:189784 AN 1977:189784 CAPLUS. **Abstract**---Treating thiazoloisoquinolinium I (R = SMe) (II) with $H_2CR^1CO_2Et$ ($R^1$ = CN, $CO_2Et$) gave mesoionic I (R = $C\text{-}R^1CO_2Et$). II treated with $MeNO_2$, AcPh, or $H_2C(CN)_2$ gave benzindolizines III ($R^2$ = MeS, $R^3 = NO_2$, H; $R^2 = NH_2$, $R^3$ = cyano, resp.) via ring opening and reclosure to give the pyrrole.
CS-27: Citing 3.



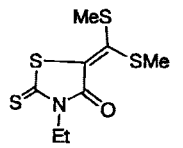
197) **Syntheses of 2-pyrone derivatives.** Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1976), 4(9), 1493-6. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 86:43501 AN 1977:43501 CAPLUS. **Abstract**---2-Pyrones I (R = H, MeO, Br, $R^1$ = CN; R = MeO, Br, $R^1 = CO_2Me$) were prepd. by condensing $4\text{-}RC_6H_4Ac$ with $(MeS)_2C:CR^1CO_2Me$ (II) in the presence of base. Cyanopyrones III ($R^2$ = 2-thienyl, 3-pyridyl, 2-quinolyl) were similarly prepd. from $R^2Ac$. Benzopyrone IV and naphthopyrone V were similarly prepd.
KD-30: Citing 4.



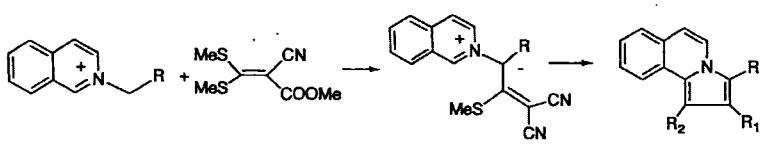
198) **Studies on quinolizine derivatives. XVI. The reaction of azacycl[3,3,3]azine derivatives. (9).** Kurata, Keiji; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1976), 24(9), 2270-2. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 86:29751 AN 1977:29751 CAPLUS. **Abstract**---Reaction of 1-azacycl[3.3.3]azine derivs. I (R = CN, $CO_2Et$) with HC.tplbond.$CCO_2Me$, $MeO_2C$.tplbond.$CCO_2Me$ and N-phenylmalimide gave the corresponding

cycl[3.3.3]azine II and III ($R^1$ = $CO_2Me$, $R^2$ = H; $R^1$ = $R^2$ = $CO_2Me$), and 3,9a-ethano-1-azacycl[3.3.3]azine derivs. IV.
Citing 1.

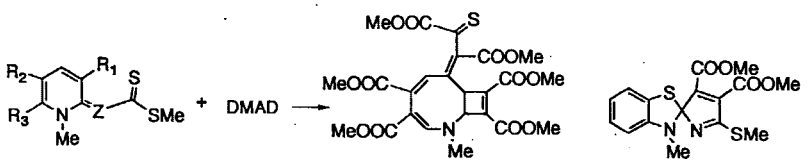
199) **Studies on heterocyclic ketenethioacetal derivatives. VII. Reactions of 3-ethyl-5-bis(methylthio)-methylene-2-thioxothiazol-4(5H)-one.** Tominaga, Yoshinori; Sone, Masakatsu; Mizuyama, Kazumichi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1976), 24(7), 1671-5. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 85:177304 AN 1976:577304 CAPLUS. **Abstract**---3-Ethyl-5-bis(methylthio)methylene-2-thioxothiazol-4(5*H*)-one (I), which was prepd. by reaction of 3-ethylrhodanine with $CS_2$ in the presence of NaOH in $Me_2SO$, reacted with nucleophilic reagents such as amines or active methylenes to give the corresponding replacement products of one or two methylthio groups in good yield.
CS-26: KD-29: Citing 4.




200) **Reaction of isoquinolinium ylides with ketenethioacetals.** Fujito, Hiroshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro.bFac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1976), 4(5), 939-42. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 85:46341 AN 1976:446341 CAPLUS. **Abstract**----Isoquinolinium allylides (I, R = $CO_2Et$, $CO_2Me$, COPh) were obtained in 25-67% yields by treatment of isoquinolinium salts II with $(MeS)_2C{:}C(CN)_2$. Similar treatment of II (R = $CO_2Et$) with $MeSC(CN){:}C(CN)_2$ gave 68% III ($R^1$ = $R^2$ = CN). Pyrroloisoquinolines (III, R = $CO_2Et$, $CO_2Me$, COPh; $R^1$ = SMe, $R^2$ = H) were obtained in 15-45% yields by treatment of II with $(MeS)_2C{:}CHNO_2$. IV (R = $CO_2Et$, $CO_2Me$) were obtained in 92 and 48% yields by treatment of II with $(MeS)_2C{:}NCN$.
KD-28: Citing 0.



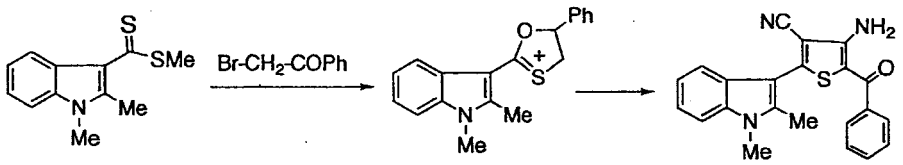

201) **Cycloaddition extrusion reaction of 2- or 4-(methylthio)thiocarbonylimino-1,2 or 1,4-dihydropyridine derivatives with dimethyl acetylenedicarboxylate.** Mizuyama, Kazumichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1976), 4(4), 705-12. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 85:21043 AN 1976:421043 CAPLUS. **Abstract**---Treatment of I ($R^1$, $R^2$, $R^3$ = H, Me, Z = NC(S)SMe) with $MeO_2CC{.}tplbond{.}CCO_2Me$ (II) in dioxane for 12 hr at room temp. gave 40-98% of the corresponding I [Z = $C(CO_2Me)C(S)CO_2Me$]. Similar treatment of 1-methyl-4-[(methylthio)thiocarbonylimino]1,4-dihydro-pyridine gave 30% of the corresponding analog whereas treatment with 2 equivs. II in DMF for 72 hr gave 40% III. Treatment of 2-[(methylthio)thiocarbonylimino]-2,3-dihydro-3-methylbenzothiazole with II at 150° for 5 hr gave 30% IV.
CS-25: Citing 1.




202) **Indole derivatives. XXVII. Syntheses and reactions of 2-indol-3-yl-1,3-oxathiolium salts.** Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1976), 4(1), 9-12. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 84:74147 AN 1976:74147 CAPLUS **Abstract**----Reaction of the dithiocarboxylates I (R = H, $R^1$ =

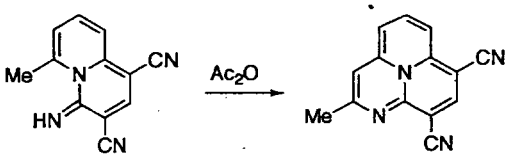
Me, Ph; R = Me, $R^1$ = Me, Ph) with $BrCH_2COPh$ in $Me_2CO$ at reflux gave the oxathiolium bromides II, which with active methylene compds. [$CH_2(CN)_2$, $MeCOCH_2CO_2Et$, $MeCOCH_2COMe$] gave the thiophenes III (R = Me; $R^1$ = Me, Ph; $R^2$ = CN, $CO_2Et$, Ac; $R^3$ = $NH_2$, Me).

CS-24.



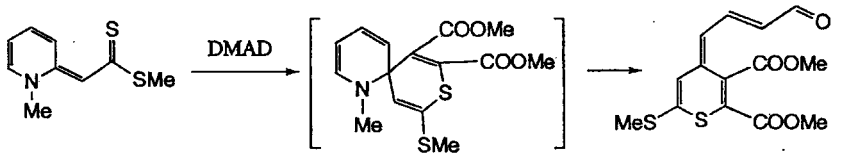

203) **Studies on quinolizine derivatives. XIV. Synthesis of azacycl[3,3,3]azine derivatives. (7).** Kurata, Keiji; Awaya, Hiroyoshi; Maseda, Chikatoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan.*Yakugaku Zasshi* (1975), **95**(12), 1431-8. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 84:105434 AN 1976:105434 CAPLUS. **Abstract**---4-Imino-6-methyl-4*H*-quinolizines I (R = H, Me; $R^1$ = $CO_2Me$, $CO_2Et$, CN) were easily obtained by condensing the appropriate 6-methyl-2-pyridineacetates II with $EtOCH:C(CN)_2$, the reaction of II with $EtOCH:C(CN)CO_2Et$ gave the Et 2-cyano-4-(6-methyl-2-pyridyl)crotonates III, and the 1-azacycl[3.3.3]azine derivs. IV (R, $R^3$ = H, Me; $R^1$ = $CO_2Me$, $CO_2Et$, CN; $R^2$ = CN, $CO_2Et$) were prepd. by cyclizing I or III with $Ac_2O$ or $EtOCH:C(CN)_2$.

Citing 3.



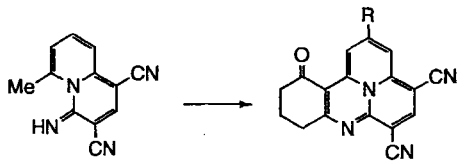

204) **The 1,4-cycloaddition reaction of enaminodithiocarboxylate derivatives with dimethyl acetylenedicarboxylate.** Kobayashi, Goro; Matsuda, Yoshiro; Tominaga, Yoshinori; Mizuyama, Kazumichi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1975), **23**(11), 2749-58. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 84:74161 AN 1976:74161 CAPLUS. **Abstract**---The enaminodithiocarboxylates I,II,III(R = Me,$CH_2Ph$),IV, and V were treated with $MeO_2CC:CCO_2Me$ to give thiopyrane, spiro(benzothiazoline), and thiazolinecyclopentadiene derivs. via 1,4-cyclo addn. and monodesulfurization, whereas reaction of lepidine and 4-picoline carboxamides VI(R = morpholino, piperidine, pyrrolidino and VII($R^1$ = morpholino, pyrrolidino) gave benzoazocine and azocine derivs. (VIII, IX, resp.).

CS-23: Citing 3.

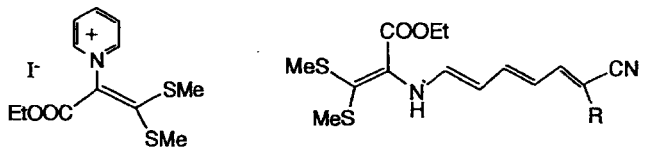



205) **Quinolizine derivatives. XV. Synthesis of azacycl[3,3,3]azine derivatives. 8.** Kobayashi, Goro; Matsuda, Yoshiro; Tominaga, Yoshinori; Maseda, Chikatoshi; Awaya, Hiroyoshi; Kurata, Keiji. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1975), **23**(11), 2759-66. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 84:59379 AN 1976:59379 CAPLUS. **Abstract**---From the reaction of 4-imino-6-methyl-4*H*-quinolizine derivs. (I) with acid anhydrides (glutaric anhydride and crotonic anhydride), the corresponding 1-azacycl[3,3,3]azine derivs. II and III (R = $CO_2Me$; $R^1$ = CN)(IV) were obtained. 1-Aza-5-oxo-2,3,4,5-tetrahydrobenzo[*b*]cycl[3,3,3]azine III (R = $R^1$ = H) was yielded, as a stable free base, by the decarboxylation of IV. 2-Methyl- and 2,5-dimethyl-1-azacycl[3,3,3]azine V (R = H, Me; $R^1$ = $R^2$ = H) which were very unstable free bases, were prepd. by the degrdn. of V ($R^1$ = $CO_2Me$, $R^2$ = CN, $R^1$ = CN, $R^2$ = $CO_2Me$). These NMR spectral data of V was interpreted in terms of a paramagnetic ring current.

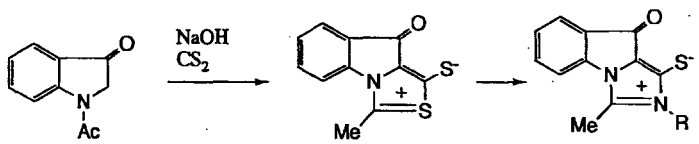
Citing 2.



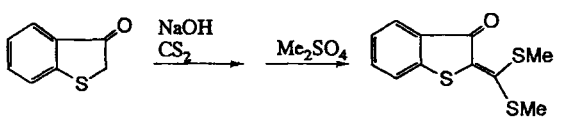
206) **Reaction of 1-[2,2-bis(methylthio)vinyl]pyridinium iodides with active methylene compounds.** Tominaga, Yoshinori; Mizuyama, Kazumichi; Miyake, Yoshinori; Fujito, Hiroshi; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1975), 3(10), 793-8. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 84:43779 AN 1976:43779 CAPLUS. **Abstract**---The pyridinium salts I (R = COPh, $CO_2Et$) reacted with $NCCH_2R^1$ ($R^1$ = CN, $CO_2Me$) in EtOH contg. $Et_3N$ to give II. I (R = H, COPh, $CO_2Et$) with $NCCH_2R^1$($R^1$ = CN, $CO_2Me$, $CONH_2$, $SO_2Ph$) in $Me_2SO$ contg. KOH gave $(MeS)_2CH:CRNHCH:CHCH:CHCH:CR^1CN$.
CS-22: KD-27: Citing 0.



207) **Indole derivatives. XXV. Syntheses of indoxyl derivatives. 5. Reaction of 1-acetyl-3-indolinone with carbon disulfide and reaction of these products.** Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1975), 95(8), 980-4. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 84:31011 AN 1976:31011 CAPLUS. **Abstract**---The reaction of 1-acetyl-3-indolinone with $CS_2$ in the presence of NaH gave anhydro-1-mercapto-3-methyl-9-oxo(9*H*)-thiazolo[3,4-*a*]indolium hydroxide. Use of excess $CS_2$ and NaOH, followed by treatment with $Me_2SO_4$ gave 3,4-dihydro-1-methylthio-3-(methylthio)thiocarbonylmethylene-imidazo[1,5-*a*]indol-9(9*H*)-one. Reaction of $CS_2$ with primary amines resulted in the formation of 2-substituted anhydro-1-mercapto-3-methyl-9-oxo(9*H*)-imidazo[1,5-*a*]indolium hydroxides I (R = benzyl, Ph, cyclohexyl $HOCH_2CH_2$, $(EtO)_2CHCH_2$), which are mesoionic compds. having an imidazo[1,5-*a*]indolium ring system. Reaction of II with hydrazines gave 10-hydroxy-3-methyl-2*H*-(1,2,4)-triazino[4,5-*a*]-indole-2-thiones (III, R = Ph, H)
CS-21: Citing 1.

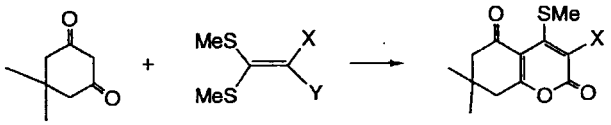


208) **Heterocyclic ketenethioacetal derivatives. VI. Synthesis and reaction of 2-bis(methylthio)-methylenebenzothiophen-3(2*H*)-one.** Tominaga, Yoshinori; Morita, Yuko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1975), 23(10), 2390-6. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 84:17052 AN 1976:17052 CAPLUS. **Abstract**---2-Bis(methylthio)methylenebenzothiophen-3(2*H*)-one, prepd. by treatment of benzothiophen-3(2*H*)-one with $CS_2$, in $Me_2SO$ contg. NaOH, reacted with nucleophilic reagents such as amines or active methylenes to give the corresponding replacement products of one or two methylthio groups in good yields.
CS-20: KD-26: Citing 4.

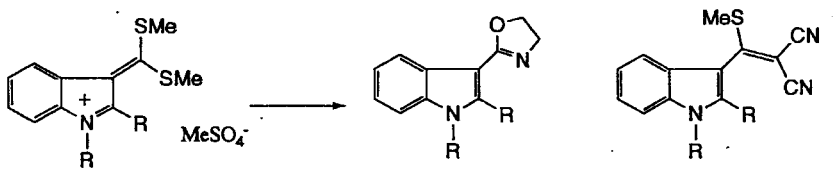


209) **Reaction of β-diketones with ketenethioacetals.** Hatada, Takayuki; Sone, Masakatsu; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1975), 95(6), 623-8. CODEN: YKKZAJ ISSN: 0031-6903. Journal

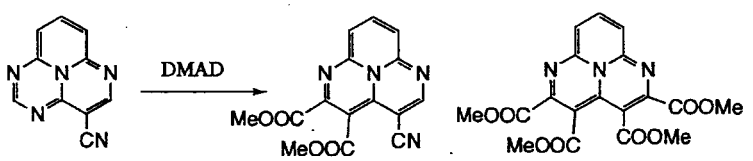
written in Japanese. CAN 83:206076 AN 1975:606076 CAPLUS. **Abstract**---By the reaction of dimedone and ketene thioacetals, corresponding substitution products, e.g. I and II, coumarin derivs., e.g. III, and quinolone deriv., IV, were synthesized. Treatment of II with conc. HCl gave IV. Reaction of $MeCOCH_2COMe$ and ketene thioacetals also gave the corresponding substitution products e.g. $HOCMe:C(COMe)C(SMe):CHNO_2$ and a pyridone deriv. Reaction of I and amines gave the corresponding substitution products. Reaction of II with conc. $NH_3$ in a sealed tube at 180° gave the substitution product V, but the reaction of II with $MeNH_2$ under the same condition gave VI.
KD-25: Citing 2.



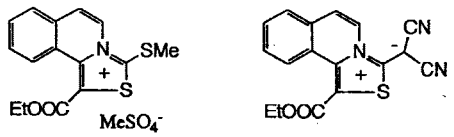
210) **Indole derivatives. XXVI. Syntheses and reactions of 3-(α,α-bismethylthiomethylene)indolenines.** Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1975), 95(9), 1073-7. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 83:206054 AN 1975:606054 CAPLUS. **Abstract**---3-(α,α-Bismethylthiomethylene)-indolenium methyl sulfates I (R = $R^1$ = Me; R = H, Me, $R^1$ = Ph), which were prepd. by the reaction of Me indole-3-dithiocarboxylates with $Me_2SO_4$, reacted with active methylene compds. to form 3-(methylthio)vinylindole derivs. II ($R^2$ = CN, $CO_2Me$) in good yields. Similarly, substitution reactions of methylthio or amino groups III (X = O $CH_2$), which were synthesized by the reaction of thioamide derivs. with MeI, with active methylene or amines gave the corresponding substituted compds.
CS-19: KD-24: Citing 1.



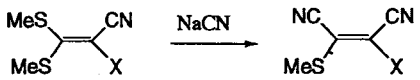
211) **Quinolizine derivatives. XIII. Synthesis of azacycl[3,3,3]azine derivatives. 6.** Kurata, Keiji; Matsuo, Miwako; Awaya, Hiroyoshi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1975), 23(7), 1629-30. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 83:178976 AN 1975:578976 CAPLUS. **Abstract**---The reaction of 4-cyano-1,3,6-triazacycl[3.3.3]azine (I) with $MeO_2CC:CCO_2Me$ in DMF gave II (R = CN, $R^1$ = H) whereas in MeCN I and $MeO_2CC:CCO_2)Me$ gave II (R = $R^1$ = $CO_2Me$).
Citing 2.



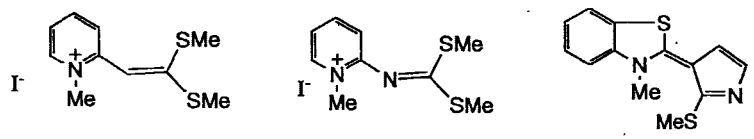
212) **Novel reaction of 3-ethoxycarbonyl-2-methylthiothiazolo[2,3-*a*]isoquinolinium sulfate with active methyl compounds.** Mizuyama, Kazumichi; Matsuo, Yoko; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1975), 3(7), 533-7. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 83:164056 AN 1975:564056 CAPLUS. **Abstract**---Thiazoloisoquinolinium sulfate (I) treated with active methyl compds. RMe (R = $NO_2$, COPh) in the presence of base gave pyrroloisoquinolines (II, $R^1$ = $NO_2$, H, resp.), presumably by formation of intermediate III and subsequent cyclization.
CS-18: Citing 0.



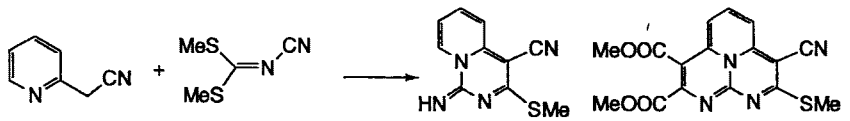
213) **Reactions of ketenethioacetal derivatives with sodium cyanide and reactions of these products with nucleophilic reagents.** Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1975), **95**(4), 378-82. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 83:58053 AN 1975:458053 CAPLUS . **Abstract**---Sodium cyanide reacted with 2-cyano-3,3-bis(methylthio)acrylonitrile and methyl 2-cyano-3,3-bis(methylthio)acrylate to give 2,3-dicyano-3-methylthioacrylonitrile and cis and trans compds. of methyl 2,3-dicyano-3-(methylthio)acrylate were obtained. Reaction of these compds. with nucleophilic reagents (amines and active methylenes) gave the corresponding compds. in which methylthio group had been substituted.
KD-23: Citing 2.



214) **Heterocyclic ketenethioacetal derivatives. V. Reactions of ketenethioacetal derivatives containing quaternary nitrogen with nucleophilic reagents.** Mizuyama, Kazumichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1975), **95**(3), 290-8. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 83:43240 AN 1975:443240 CAPLUS. **Abstract**---The reactions of heterocyclic ketenethioacetal derivs., contg. a quaternary N as an electron-attracting group, with nucleophilic reagents (amines and active methylenes) gave the corresponding substituted compds. By the application of these reactions, fulvalene I, imidazolines, e.g. II, and oxazoline derivs., e.g. III, were obtained.
CS-17: KD-22: Citing 2.

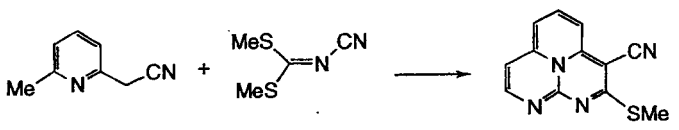


215) **Quinolizine derivatives. X. Synthesis of cyclazine derivatives and their reactions.** Awaya, Hiroyoshi; Maseda, Chikatoshi; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1975), **95**(1), 13-16. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 83:9966 AN 1975:409966 CAPLUS . **Abstract**---1-Cyano-4-imino-2-methylthio-4*H*-pyrido[1,2-*c*]pyrimidine (I) was obtained from 2-pyridineacetonitrile and dimethyl cyanamidedithiocarboxylate. The reaction of I with morpholine, $Ac_2O$, and MeI gave the corresponding products (II, III, and IV), while I or 3-cyano-4-imino-4*H*-pyrido[1,2-*a*]pyrimidine and dimethyl acetylenedicarboxylate afforded 1,9-diazacycl[3.3.3]azine deriv. (V) and 1,4-diazacycl[3.3.3]azine deriv. (VI). The reaction of V with morpholine resulted in the formation of corresponding products (VII and VIII).
KD-21: Citing 4.

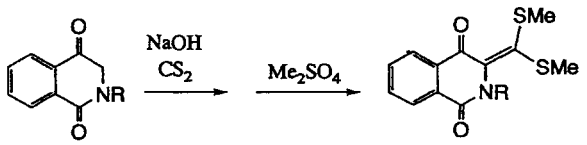


216) **Quinolizine derivatives. XII. Synthesis of diazacycl[3.3.3]azine derivatives.** Matsuo, Miwako; Awaya, Hiroyoshi; Maseda, Chikatoshi; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1974), **22**(11), 2765-6. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 82:125340 AN 1975:125340 CAPLUS. **Abstract**---6-Methyl-2-pyridineacetonitrile was treated with MeSCR:NCN (R = SMe, OEt) to give the pyridopyrimidine I, which with $EtOCH:C(CN)_2$ gave the diazacyclazine II ($R^1$ = H). The reaction of I with $Ac_2O$ gave II ($R^1$ = Me).

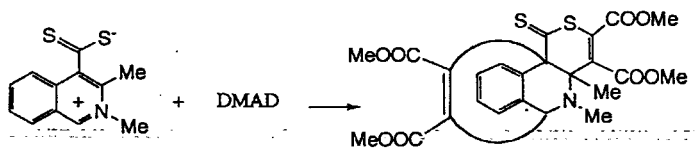
KD-20: Citing 2.



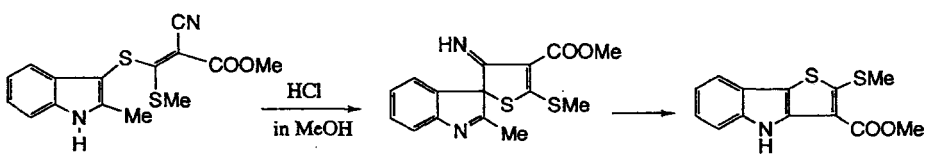
217) **Heterocyclic ketenethioacetal derivatives. IV. Reactions of 1,2,3,4-tetrahydro-1,3-dioxoisoquinoline and 1,2,3,4-tetrahydro-1,4-dioxoisoquinoline with ketene thioacetals and reaction of these products.** Ueno, Seiichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1974), 22(11), 2624-34. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 82:72760 AN 1975:72760 CAPLUS. **Abstract**---Reaction of 1,3-dioxo- or 1,4-dioxo-1,2,3,4-tetrahydroisoquinolines with ketene thioacetals, e.g., $(MeS)_2C{:}C(CN)CO_2Me$, gave the corresponding substitution products, e.g., I, in good yields. The application of these reactions afforded pyrano[2,3-*c*]isoquinoline and pyrrolo[1,2-*b*]isoquinoline, III (Z = O), derivs. The reaction of I and related compds. with amines afforded recyclized products, 2-benzopyranopyrano[3,4-*b*]pyridine derivs., e.g. II. The reaction of III (Z = O) with amines gave amino derivs., e.g., III ($Z = NNH_2$). The reaction of IV with aminoacetal afforded an aminoacetal deriv. which was treated with HCl to give a cyclized product V. The cyclization of derivs. Of III (Z = O) with Et orthoformate or $HCO_2H$ gave pyrimidine derivs.
CS-16: KD-19: Citing 4.



218) **1,4-Dipolar addition of 2,3-dimethylisoquinolinium-4-dithiocarboxylate with dimethyl acetylenedicarboxylate.** Mizuyama, Kazumichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1974), 2(5), 611-14. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 82:43213 AN 1975:43213 CAPLUS . **Abstract**---Cycloaddn of the isoquinolinium dithiocarboxylate I with $MeO_2CC.tplbond.CCO_2Me$ (1:2) gave the ethenothiapyranoisoquinoline II.
CS-15: Citing 1.

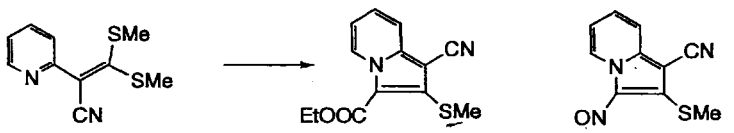


219) **Indole derivatives. XXIV. Reactions of methyl 2-cyano-3-(2-substituted indol-3-yl)thio-3-methylthioacrylates.** Kisaki, Shunichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1974), 22(10), 2246-51. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 82:43128 AN 1975:43128 CAPLUS. **Abstract**---Reaction of Me 2-cyano-3-(2-substituted indol-3-yl)thio-3-methylthioacrylates I (R = MeS, $R^1$ = H, Me, Ph) with various nucleophilic reagents (amines, active methylene compds.) gave substitution of the methylthio or the indolylthio group. Treatment of I (R = MeS, $PhCH_2NH$) with 10% HCl gave thieno[3,2-*b*]indoles II (R = MeO, $NH_2$; $R^1$ = MeS, PhNH).
KD-18: Citing 3.

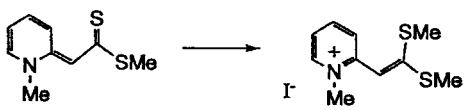


220) **Synthesis of indolizine derivatives and their reactions.** Maseda, Chikatoshi; Sone, Masakatsu; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ.,

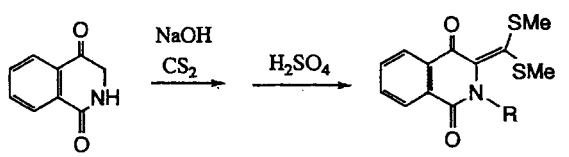
Nagasaki, Japan. *Yakugaku Zasshi* (1974), 94(7), 839-43. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 81:152106 AN 1974:552106 CAPLUS. **Abstract**---Indolizine derivs. I (R = CO2Et, COMe, COPh, CH:CHCO$_2$Et, R$^1$ = CN) and II (R = CO$_2$Et, COMe, COPh, CH:CHCO$_2$Et) were synthesized by the reaction of α-[bis(methylthio)methylene]-2-pyridineacetonitrile (III) and di-Me *N*-(2-pyridyl) dithiocarbimidate with α-haloketones and Et γ-bromocrotonate. Reaction of III with nitromethane gave I (R = NO, R$^1$ = CN). di-Me 1-carbamoyl-2-methyl thiocycl[3.2.2]azine-3,4-dicarboxylate IV was obtained from I (R = H, R$^1$ = CONH$_2$) and MeO$_2$CC.tplbond.CCO$_2$Me.
KD-17: Citing 8.




221) **Heterocyclic ketenethioacetal derivatives. III. Syntheses of enaminodithiocarboxylates and their conversion into ketenethioacetal derivatives.** Mizuyama, Kazumichi; Tominaga, Yoshinori; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1974), 94(6), 702-7. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 81:135915 AN 1974:535915 CAPLUS. **Abstract**---Enaminodithiocarboxylates I-IV (R = CHCS$_2$Me) were prepd. by treating 1,2-dimethylquinolinium iodide, 1,2-dimethylpyridinium iodide, 1,4-dimethylpyridinium iodide (V), and 1,2-dimethylbenzothiazolium iodide with CS$_2$ in the presence of a base. The corresponding ketene thioacetals, e.g., VI, were prepd. by the alkylation of I-IV. Treating V with CS$_2$ and NaOH introduced 2 moles CS$_2$ into the Me group at 4-position to produce 1,4-dihydro-1-methyl-4-(3,5-dithioxo-1,2-dithiolan-4-ylidene)pyridine.
CS-14: KD-16: Citing 1.

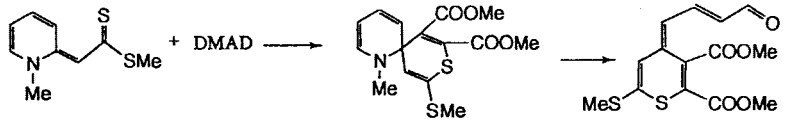



222) **Heterocyclic ketene thioacetal derivatives. II. Reaction of 1,4-dioxo-1,2,3,4-tetrahydroisoquinoline with carbon disulfide.** Ueno, Seiichi; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1974), 94(5), 607-12. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 81:120391 AN 1974:520391 CAPLUS. **Abstract**---1,4-Dioxo-1,2,3,4-tetrahydroisoquino-line treated with CS$_2$ and Me$_2$SO$_4$ in ammonia water gave Me 1,4-dioxo - 1,2,3,4-tetrahydroisoquinoline-3-dithiocarboxylate (I) which was further methylated with MeI to 3-bis(methylthio)-methylene-1,4-dioxo-1,2,3,4-tetrahydroisoquinoline (II). I and alkyl bromoacetate in the presence of potassium carbonate gave 1-alkoxycarbonyl-3-alkoxycarbonylmethylthio-5-oxo-4*H*,5*H*-thieno[3,4-*c*]isoquinolines III (R = Me, Et). I was also converted to di-Me 6,11-dioxo-1-methylthio-3,4,6,11-tetrahydro[1,4]thiazino[4,3-*b*]isoquinoline-3,4-dicarboxylate (IV) by the action of MeO$_2$CC.tplbond.CCO$_2$Me. Treatment of I or II with phosphorus pentasulfide gave 3,3,4,5-tetrahydro-1,2-dithiolo[4,3-*c*]isoquinoline-3,5-dithione. The reaction of II with amines gave the corresponding amino derivs., e.g. V. The reaction of II and NaCN gave 3-[cyano(methylthio)]-methylene-1,4-dioxo-1,2,3,4-tetrahydroisoquinoline, which reacted with H$_2$NNH$_2$.H$_2$O to form 3,6-dioxo-4-methylthio-2,3,5,6-tetrahydropyridazino[4,3-*c*]isoquinoline VI.
CS-13: KD-15: Citing 2.

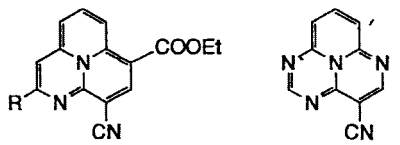



223) **Reaction of 1-methyl-2-(methylthio)thiocarbonylmethylene-1,2-dihydropyridine with dimethyl acetylenedicarboxylate.** Tominaga, Yoshinori; Mizuyama, Kazumichi; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1974), 22(7), 1670-1. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 81:120390 AN 1974:520390 CAPLUS. **Abstract**---The title reaction of the pyridine I with MeO$_2$CC.tplbond.CCO$_2$Me gave 15% thiopyran II.

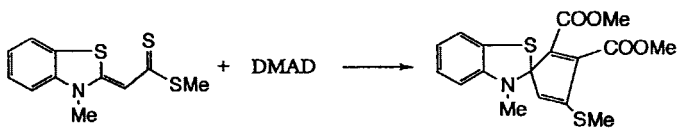
CS-12: Citing 1.



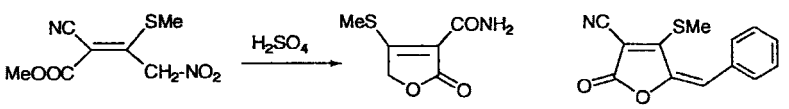

224) **Quinolizine derivatives. IX. Synthesis of azacycl[3.3.3]azine derivatives.** Awaya, Hiroyoshi; Maseda, Chikatoshi; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1974), 22(6), 1424-6. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 81:105458 AN 1974:505458 CAPLUS. **Abstract**---Cyclization of Et 6-methyl-2-pyridineacetate, with $EtOCH:C(CN)_2$ gave I (R = H, $R^2 = CO_2Et$) and II [$R^2 = CO_2Et$, $R^3$ = H, $CH:C(CN)_2$]. Cyclization of 6-methyl-2-pyridine-acetonitrile and 2,6-diaminopyridine with $EtOCH:C(CN)_2$ gave only II ($R^2$ = CN, $R^3$ = H) and III resp. II ($R^2 = CO_2Et$, CN, $R^3$ = H) cyclized with $Ac_2O$ to give I (R = Me, $R^2 = CO_2Et$, CN).
Citing 3.




225) **Reaction of methyl 2,3-dihydro-3-methyl-2-methylene-benzothiazole-α-dithiocarboxylate with dimethyl acetylenedicarboxylate.** Kobayashi, Goro; Matsuda, Yoshiro; Tominaga, Yoshinori; Mizuyama, Kazumichi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Heterocycles* (1974), 2(3), 309-13. CODEN: HTCYAM ISSN: 0385-5414. Journal written in English. CAN 81:49611 AN 1974:449611 CAPLUS. **Abstract**---Desulfurization and ring contraction during the Diels-Alder reaction of the thiocarbonyl dienes I (R = Me, $CH_2Ph$) and II with $MeO_2CC.tplbond.CCO_2Me$, gave the spiro[banzothiazoline-2(3*H*),1'-[2,4]cyclopentadienes] (III, R = Me, $CH_2Ph$) and spiro[cyclopentadiene-thiazoline] (IV), resp.
CS-11: Citing 0.

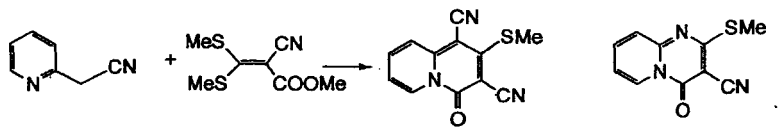



226) **Reactions of 1,1-bismethylthio-2-nitroethylene. IV. Syntheses and reactions of 4-methylthio-2-buten-4-olide derivatives.** Sone, Masakatsu; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1974), 22(3), 617-22. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 81:3306 AN 1974:403306 CAPLUS. **Abstract**---Treatment of methyl 2-cyano-3-(methylthio)-4-nitrocrotonate with $H_2SO_4$ gave 2-carbamoyl-3-(methylthio)-2-buten-4-olide (I) in a good yield. The methylthio group of I was replaced by nucleophilic reagents such as amines or active methylene compds. Condensation reaction of I as a nucleophilic reagent with various reagents having a formyl or ketone group gave corresponding condensation products. Reaction of I with quinoline 1-oxide gave 2-carbamoyl-3-(methylthio)-4,4-bis(2-quinolyl)-2-buten-4-olide (II).
KD-14: Citing 4.

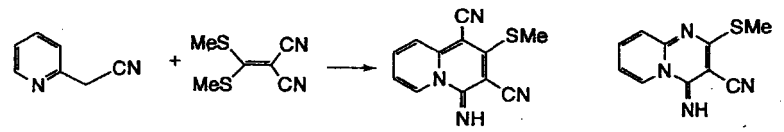



227) **Quinolizine derivatives. VIII. Reaction of 3-cyano-2-methylthio-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine and 3-cyano-4-imino-2-methylthio-4*H*-pyrido[1,2-*a*]pyrimidine.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori; Maseda, Chikatoshi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1974), 94(1), 44-9. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 80:108477 AN 1974:108477 CAPLUS. **Abstract**---Reaction of 3-cyano-2-(methylthio)-4-

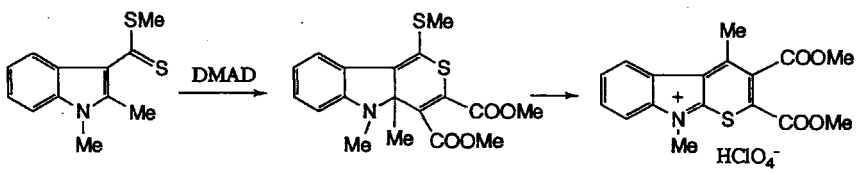
oxo-4*H*-pyrido[1,2-*a*]pyrimidine (I) and $(EtO_2C)_2CH_2$ gave the corresponding substituted product (II). Reaction of I with polyphosphoric acid easily gave the decyanated product (III), while reaction of I with $NaBH_4$ gave IV. Reaction of 3-cyano-4-imino-2-(methylthio)-4*H*-pyrido[1,2-*a*]pyrimidine (V) and amines resulted in addn. of amino to the 4-position yielding VI. Reaction of V with $H_2SO_4$ gave I, that with MeI gave the *N*-methyl compds. (VII), that with NaOH the substituted product VIII, and that with NaBH4, the tetrahydro compd. IX.
KD-13: Citing 3.



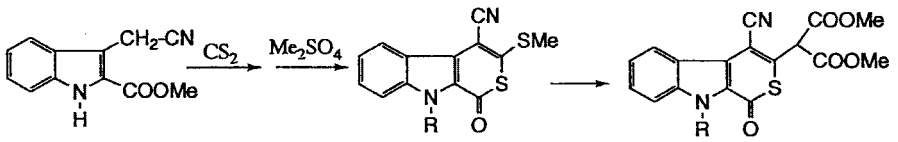
228) **Quinolizine derivatives. VIII. Synthesis of cyclazine derivatives and their reactions.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori; Maseda, Chikatoshi; Awaya, Hiroyoshi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1974), 94(1), 50-4. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 80:108339 AN 1974:108339 CAPLUS. **Abstract**---1,3-Dicyano-4-imino-2-methylthio-4*H*-quinolizine (I) was prepd. from 2-pyridineacetonitrile and 2-cyano-3,3-bis(methylthio)acrylonitrile, and the reactivity of I was examd. The reaction of I amines gave products with addn. of the amines to the C:NH double bond, while the reaction with MeI and $Ac_2O$ gave the corresponding *N*-Me and *N*-Ac derivs. The reaction of I or 1,3-dicyano-4-mino-4*H*-quinolizine (II) with di-Me acetylenedicarboxylate gave 1-azacycl[3.3.3.]azine derivs. (III, IV), and the reaction of III with amines, such as $PhCH_2NH_2$, gave the corresponding substituted products, such as V.
KD-12: Citing 3.



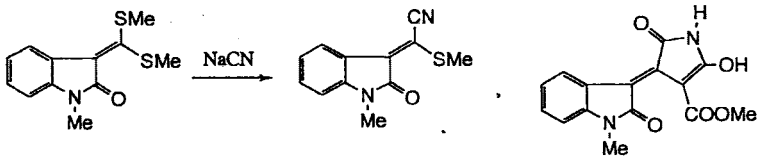
229) **Indole derivatives. XXIII. Diels-Alder reaction of 3-indoledithiocarboxylic acid derivatives and dimethyl acetylenedicarboxylate and reactions of their products.** Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1973), 21(12), 2770-5. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 80:82737 AN 1974:82737 CAPLUS. **Abstract**---Diels-Alder reaction of I ($R^1$ = H, Me; $R^2$ = Me, Ph; $R^3$ = Me, $CH_2CN$) with $MeO_2CC.tplbond.CCO_2Me$ gave II. Treatment of II ($R^1$ = H, $R^2$ = $R^3$ = Me) with $PhCH_2NH_2$ gave the corresponding diamide, whereas treating with $H_2NNH_2$ gave III.
CS-10: Citing 1.



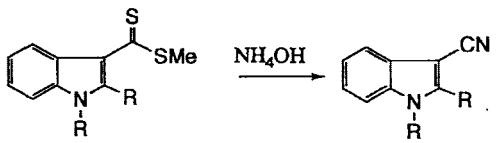
230) **Indole derivatives. XXI. Reactions of 3-(methylthio)thiapyrano[3,4-*b*]indol-1-ones and 4-(methylthio)pyrano[3,2-*b*]indol-2-ones with active methylenes.** Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1973), 93(11), 1523-6. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 80:59885 AN 1974:59885 CAPLUS. **Abstract**---Reaction of 3-(methylthio)thiapyrano[3,4-*b*]indol-1-ones I (R = H, Me; $R^1$ = SMe) and active methylenes gave I [R = H, Me; $R^1$ = $CH(CN)CO_2Me$, $CH(CN)CO_2Et$, $CH(CO_2Et)_2$]. Reaction of 4-(methylthio)pyrano[3,4-*b*]indol-2-one (II, R = SMe) with active methylenes gave II [R = $CH(CO_2Me)_2$, $CH(CO_2Et)_2$, $CH(COMe)CO_2Et$].
CS-9: Citing 1.



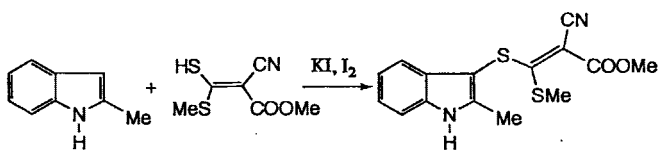
231) **Indole derivatives. XX. Synthesis and reactions of 3-[cyano(methylthio)methylene]oxindole.** Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan.*Yakugaku Zasshi* (1973), **93**(11), 1520-2. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 80:47770 AN 1974:47770 CAPLUS. **Abstract**---Reaction of NaCN with 3-[bis(methylthio)methylene]oxindole (I) afforded 3-[cyano(methylthio)methylene]oxindole (II). The reaction of II with nucleophilic reagents such as amines and active methylene compds. gave the corresponding products formed by substitution of the methylthio group of II.
CS-8: KD-11: Citing 1.



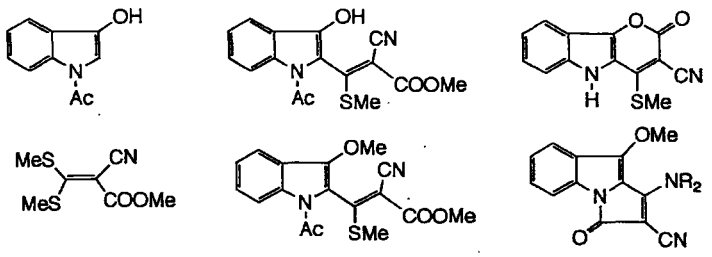
232) **Indole derivatives. XIX. New synthetic methods of 3-cyanoindole derivatives from methyl 3-indoledithiocarboxylate derivatives.** Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan.*Yakugaku Zasshi* (1973), **93**(11), 1433-6. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 80:47769 AN 1974:47769 CAPLUS. **Abstract**---3-Cyanoindoles (I) were synthesized in a good yield by the reaction of Me 3-indoledithiocarboxylates and aq. $NH_3$. The reaction of 2-hydroxy-3-indoledithiocarboxylates and $NH_2OH$ also afforded the corresponding I.
CS-7: Citing 1.



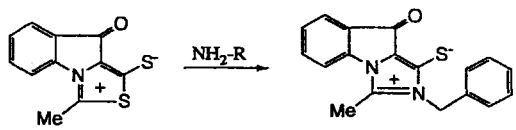
233) **Indole derivatives. XXII. Synthesis and reactions of methyl 3-(2-substituted 3-indolyl)thio-2-cyano-3-methylthioacrylates.** Kobayashi, Goro; Tominaga, Yoshinori; Kisaki, Shunichi; Sone, Masakatsu; Ueno, Seiichi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1973), **21**(10), 2344-5. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 80:47759 AN 1974:47759 CAPLUS. **Abstract**---The indolylthioacrylates I(R = H, Me, Ph) were prepd. by treating the 3-iodoindoles with KSC(SMe):C(CN)$CO_2$Me. On treatment with HCl-MeOH I cyclized to the spirothiophene indoles II, which rearranged on prolonged treatment to 2-methylthio-3-methoxycarbonyl-thieno[3,2-*b*]indole and $RCO_2H$.
KD-10: Citing 2.



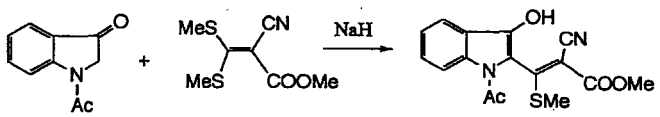
234) **Indole derivatives. XVII. Synthesis of indoxyl derivatives. 3. Reactions of 3-hydroxy-2-(1-methylthiovinyl)indole derivatives with amines.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori; Okamura, Tatehiko; Itamura, Akemi. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1973), **93**(8), 964-70. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 79:115396 AN 1973:515396 CAPLUS. **Abstract**---Pyrano- and pyrroloindolones (I, II, R = e.g., $PhCH_2NH$, morpholino, pyrrolidino; $R^1$ = OH, OMe, $NHCH_2Ph$, pyrrolidino) were prepd. by treating III ($R^2$ = H, Ac, p-$MeC_6H_4SO_2$) with the amines RH. III ($R^2$ = p-$MeC_6H_4SO_2$) with $NH_2NH_2$ gave IV.
KD-9: Citing 2.



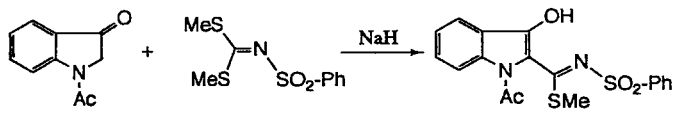
235) **Indole derivatives. XV. Synthesis of indoxyl derivatives. 1. Crystal and molecular structure of anhydro-2-benzyl-1-mercapto-3-methyl-9-oxo-(9*H*)-imidazo[1,5-*a*]indolium hydroxide.** Tominaga, Yoshinori; Tamura, Chihiro; Sato, Sadao; Hata, Tadashi; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1973), **21**(8), 1651-7. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 79:109104 AN 1973:509104 CAPLUS. **Abstract**---The new mesoionic compd., anhydro-2-benzyl-1-mercapto-3-methyl-9-oxo-9*H*-imidazo[1,5-*a*]indolium hydroxide, was synthesized by the reaction of 1-acetyl-3-indolinone, $CS_2$, and benzylamine. The structure was detd. by x-ray anal. The crystals are monoclinic, a 11.58, b 8.52, c 15.50 .ANG., β 102.7°, and space group P21/c. The intensities of all independent reflections were measured with a Rigaku auto diffractometer and a total of 887 were collected and employed for structure detn. by the heavy-atom method. The final R factor is down to 0.067 by a block diagonal least-squares refinement. The mesoionic imidazolium ring system is almost planar. The C-S bond of 1.678 .ANG. agrees well with the accepted value of 1.78 .ANG.; Me group of 1.449 .ANG. attached to an imidazolium ring indicates some double bond character.
CS-6: Citing 0.



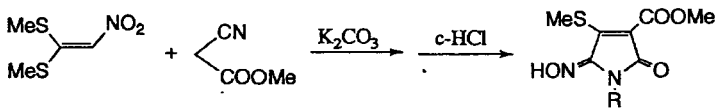
236) **Indole derivatives. XVI. Synthesis of indoxyl derivatives. 2. Reactions of 1-acetyl-3-indolinone with ketenethioacetal derivatives.** Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1973), **21**(8), 1658-66. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 79:105109 AN 1973:505109 CAPLUS. **Abstract**---Reaction of 1-acetyl-3-indolinone with $(MeS)_2C{:}CRCO_2Me$ (R = CN, $CO_2Me$) in presence of NaH gave the 3-indolinols (I). Heating I (R = CN) at 180-200° gave the pyranoindolone (II) while refluxing with 10% HCl in MeOH gave the pyrroloindolone (III).
KD-8: Citing 6.



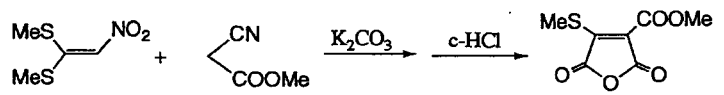
237) **Indole derivatives. XVIII. Synthesis of indoxyl derivatives. 4. Reaction of 1-acetyl-3-indolinone with *N*-bis(methylthiomethylene)benzenesulfonamides and reaction of these products with nucleophilic reagents.** Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1973), **93**(8), 971-6. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 79:105029 AN 1973:505029 CAPLUS. **Abstract**---1-Acetyl-3-indolinone was treated with *N*-bis(methylthio)methylene benzenesulfonamides in the presence of a base to give compds. such as I and II, depending on the reaction conditions. Reaction of I and II with nucleophilic reagents such as amines and active methylenes afforded substitution products corresponding to the reagent used. Using these products, indole-condensed ring compds., 1-(*p*-toluenesulfonylamino)-10-(*p*-toluenesulfonyloxy)pyrazino [1,2-*a*]indole and 1-(*p*-toluenesulfonylamino)-2-cyano-3*H*-pyrrolo[1,2-*a*]-indol-3-one, were synthesized.
KD-7: Citing 0.



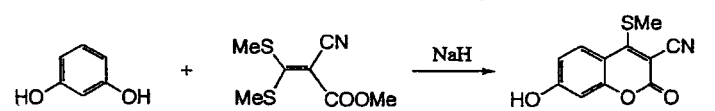
238) **Reaction of 1-nitro-2,2-bis(methylthio)ethylene. II. Synthesis of 2-hydroxyimino-3-methylthio-5-oxopyrroline derivatives.** Sone, Masakatsu; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Chemical & Pharmaceutical Bulletin* (1973), **21**(8), 1667-75. CODEN: CPBTAL ISSN: 0009-2363. Journal written in English. CAN 79:105024 AN 1973:505024 CAPLUS. **Abstract**---2-(Hydroxyimino)-3-(methylthio)-5-oxo-pyrrolines (I, R = $CO_2Me$, $CONH_2$, Ph; $R^1$ = H) were prepd. by refluxing $RC(CN):C(SMe)CH_2NO_2$ (II) in MeOH or EtOH. Reaction of II (R = $CO_2Me$) with equimolar amts. of amines $R^2H$ $R^2$ = $PhCH_2NH$, $HOCH_2CH_2NH$, $(EtO)_2CHCH_2NH$, $EtO_2CCH_2NH$, $NCCH_2CH_2NMe$, piperidino gave the pyrrolinecarboxylates (III). Active methylene compds. such as $NCCH_2CN$, $NCCH_2CO_2Et$ etc. reacted with I (R = $CO_2Me$, $R^1$ = Me) to give IV ($R^3$ = $R^4$ = CN, $R^3$ = CN, $R^4$ = $CO_2Et$ etc.).
KD-6: Citing 6.



239) **Reaction of 1-nitro-2,2'-bis(methylthio)ethylene. III. Reaction of methyl 1-cyano-2-methylthio-3-nitrocrotonate with hydrochloric acid.** Sone, Masakatsu; Tominaga, Yoshinori; Natsuki, Reiko; Matsuda, Yoshiro; Kobayashi, Goro. Fac. Pharm. Sci., Nagasaki Univ., Nagaski, Japan. *Yakugaku Zasshi* (1973), **93**(8), 1008-13. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 79:105018 AN 1973:505018 CAPLUS. **Abstract**---Methyl 1-cyano-2-(methylthio)-3-nitrocrotonate was reacted with hydrochloric acid under various conditions to give 2,5-dihydro-2-(hydroximino)-5-imino-4-(methoxycarbonyl)-3-(methylthio)furan monohydrochloride, 2,5-dihydro-2-(hydroximino)-4-(methoxycarbonyl)-3-(methylthio)furan, and α-(methylthio)-β-(methoxycarbonyl)maleic anhydride. The mutual relationship of these products was clarified.
KD-5: Citing 4.

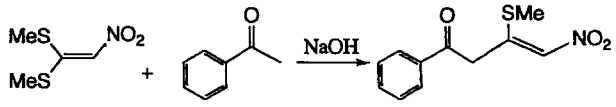


240) **Coumarin derivatives. I. Synthesis of 3-cyano-7-hydroxy-4-methylthiocoumarin.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1973), **93**(7), 836-40. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 79:91910 AN 1973:491910 CAPLUS. **Abstract**---3-Cyano-7-hydroxy-4-methylthiocoumarin (I) was prepd. by the reaction of $(MeS)_2C:C(CN)CO_2Me$ with o-$(HO)_2C_6H_4$ in the presence of NaH. I was converted to 7-hydroxycoumarin.
KD-4: Citing 2.

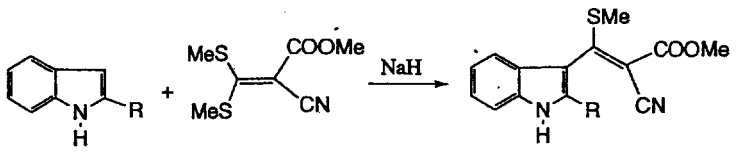


241) **Reaction of 1-nitro-2,2'-bis(methylthio)ethylene. I. Reaction with active methylene compounds.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori; Sone, Masakatsu. Fac. Pharm. Sci., Nagasaki Univ., Bunkyo, Japan. *Yakugaku Zasshi* (1973), **93**(5), 612-18. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 79:41826 AN 1973:441826 CAPLUS **Abstract**---Examns. were made on the reaction of 2,2-bis(methylthio)-1-nitroethylene with active methylenes (acetophenone derivatives, methyl cyanoacetate, dimedone, hydroxindole, rhodanine, 1,1-dioxo-2,3-dihydrobenzo[*b*]-thiophen-3(2*H*)-one), and with indole derivs. as an intramol. enamine. It was found that the use of THF as a solvent and sodium hydride as a base produced substitution reaction of the two methylthio groups while the use of dimethyl sulfoxide as a solvent and sodium hydroxide as a base resulted in the reaction of only one methylthio group. The reaction of compds. obtained by the above reaction with amines was also carried out.

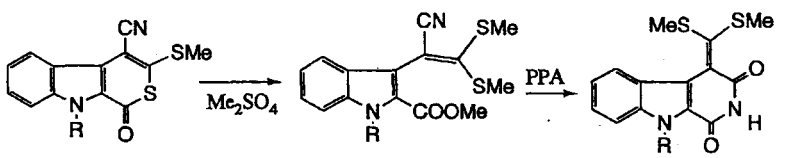
KD-3: Citing 1.



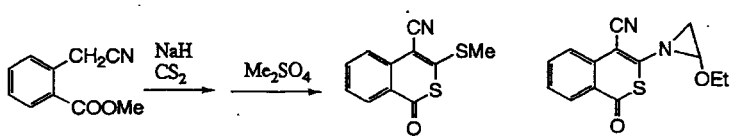

242) **Indole derivatives. XIV. Synthesis of 3-(2-cyano-1-methylthiovinyl)indole derivatives and reactions of these derivatives with some nucleophilic reagents.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1972), 92(12), 1468-72. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 78:97425 AN 1973:97425 CAPLUS. **Abstract**---Reaction of indole derivs. with ketenethioacetals, in the presence of NaH or NaOH, resulted in the formation of 3-(2-cyano-1-methylthiovinyl)indole derivs. e.g. I. Reaction of the indole derivs. with various nucleophilic reagents (amines, active methylene compds., sodium cyanide) resulted in the formation of products by substitution of the methylthio group.]
KD-2: Citing 3.




243) **Indole derivatives. XIII. Reaction of 1-(1-methyl-2-methoxycarbonylindol-3-yl)-2,2-bismethylthioacrylonitrile.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori. Pharm. Fac., Univ. Nagasaki, Nagasaki, Japan. *Yakugaku Zasshi* (1972), 92(6), 713-18. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 77:88363 AN 1972:488363 CAPLUS. **Abstract**—2,2-Bis(methylthio)-1-(1-methyl-2-methoxycarbonylindol-3-yl)acrylonitrile (I) reacted with amines, to give β-carboline derivs. 1,3-Dioxo-β-carboline derivs. were obtained by treatment of I with polyphosphoric acid. 1,3-Dioxo-β-carboline treated with $CS_2$ and NaH and alkylated with $Me_2SO_4$ gave 1,3-dioxo-1,3,4-trihydro-2,9-dimethyl-4-[bis(methylthio)methylene]-β-carboline. Reaction of 3-cyanomethylindole derivs. and ketene thioacetals afforded II (R = Me, Et; $R^1$ = $CO_2Me$, CN), 1-cyano-2-(methylthio)-3-nitro-4-hydroxycarbazole, and 1-oxo-1,2,9-trihydro-3-methylthio-4-cyano-β-carboline.
CS-5: KD-1: Citing 1.

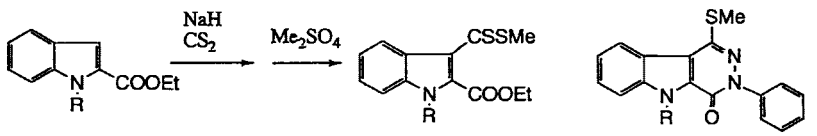



244) **Synthesis of 3-methylthio-4-cyanothiosisocoumarin derivatives and their reactions. 1.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Yamaguchi, Hiroyuki; Tominaga, Yoshinori. Pharm. Fac., Univ. Nagasaki, Nagasaki, Japan. *Yakugaku Zasshi* (1972), 92(4), 449-53. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 77:61747 AN 1972:461747 CAPLUS. **Abstract**—Treatment of o-$RCH_2C_6H_4CO_2Me$ (I, R = CN, $CO_2Me$) with $CS_2$ in $Me_2SO$ contg. NaH gave mercapto-2-thioisocoumarins (II, R = CN, $CO_2Me$, $R^1$ = SH), resp. Similarly, I, $CS_2$, and $Me_2SO_4$ gave 54% II (R = CN, $R^1$ = MeS) (III) and 48% II (R = $CO_2Me$, $R^1$ = MeS). Amination of III with $H_2N(CH_2)_2NEt_2$ or aziridine gave 78% II (R = CN, $R^1$ = 1-aziridinyl).
CS-4: Citing 2.

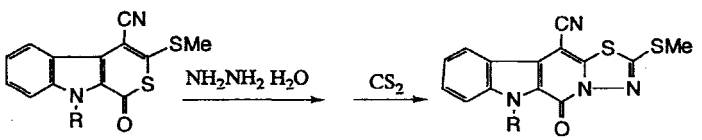



245) **Indole derivatives. XII. Reaction of indole-2-carboxylic acid derivatives with carbon disulfide.** Kobayashi, Goro; Matsuda, Yoshiro; Natuki, Reiko; Tominaga, Yoshinori. Fac. Pharm. Sci., Nagasaki Univ., Nagasaki, Japan. *Yakugaku Zasshi* (1971), 91(11),1164-73. CODEN: YKKZAJ ISSN: 0031-6903. Journal

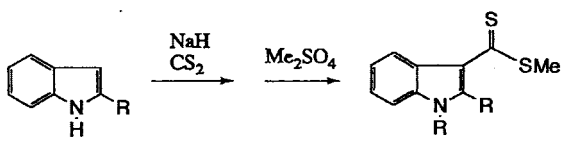
written in Japanese. CAN 76:46033 AN 1972:46033 CAPLUS.---**Abstract**---Application of NaH, $CS_2$, or $Me_2SO_4$ to indole derivs. having an electron attracting group at C-2 of the indole ring, resp. afforded Me indole-3-dithiocarboxylate, indole-3-thiolo ester, or imidazo-[3,4-*a*]indole derivs. Substitution of methylthio group in these compds. with amines was carried out and thioamides and amide derivs. were obtained. Reaction of these compds. with hydrazines afforded pyridazino[4,5-*b*]indole derivs. Reaction of these compds. with $PhNHNH_2$ gave a new type of specific reaction of the hydrazine with the thiocarbonyl group of dithiocarboxylate.
CS-3: Citing 0.




246) **Indole derivatives. XI. Reactions of 3-indolylacetonitrile derivatives with carbon disulfide.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori. Pharm. Fac., Univ. Nagasaki, Nagasaki, Japan. *Yakugaku Zasshi* (1971), **91**(2), 203-9. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 74:125507 AN 1971:125507 CAPLUS. **Abstract**---In the reaction of 3-indoleacetonitrile derivs. and $CS_2$, indole derivs. without a substituent in 2-position afford ketene thioacetal derivs. (I) while those with a carbonyl or carboxyl in 2-position form condensed thiopyrone ring, thiopyrano[3,4-*b*]indole derivs. (II). Substitution of the methylthio group in I and II with amines was carried out. In the reaction of II and hydrazine hydrate, the product was a ring-cleaved 2-(2-hydrazinocarbonyl-3-indolyl)-3-hydrazino-3-mercaptoacrylonitrile (III) whose treatment with ketone or aldehyde afforded a cyclized product, 4-cyano-3-mercaptopyrido[3,4-*b*]indole deriv. Treatment of III with $CS_2$ and $Me_2SO_4$ resulted in 5-cyano-3-methylthio-1-oxo-1,3,4-thiadiazolo[2,3-*b*]harman.
CS-2: Citing 0.




247) **Indole derivatives. X. Synthesis of methyl indole dithiocarboxylates and their reaction with amines.** Kobayashi, Goro; Matsuda, Yoshiro; Natsuki, Reiko; Tominaga, Yoshinori. Pharm. Fac., Univ. Nagasaki, Nagasaki, Japan. *Yakugaku Zasshi* (1970), **90**(10), 1251-7. CODEN: YKKZAJ ISSN: 0031-6903. Journal written in Japanese. CAN 74:3570 AN 1971:3570 CAPLUS. **Abstract**---Methyl-indoledithio-carboxylate derivs. were synthesized by the reaction of NaH and $CS_2$ on indole derivs., followed by treatment with $Me_2SO_4$. Substitution reactions were carried out between a methylthio group in these compds. and various amines to obtain thioamide derivs. Pyridazino[4,5-*b*]indole derivs. were synthesized by these reactions.
CS-1: Citing 3.



# Reviews

1) The synthesis and properties of polycyclic aromatic thiophenes and related heterocycles occurring in coal-products.
R. N. Castle, M. L. Tedjamulia, Y. Tominaga, R. Pratap, M. Sugiura, H. Kudo, M. L. Lee, M. Iwao, R. D. Thompson, G. E. Matin, R. T. Gampe, Jr., M. J. Musmar, M. R. Willcott, S. L. Smith, W. J. Layton, R. E. Hurd, and L. F. Johnson.
*Lectures in Heterocyclic Chemistry*, **VII**, 1-50 (1984).

2) ケテンジチオアセタールを利用するインドリジン誘導体およびそれら関連化合物の合成。
富永義則、松田芳郎
*有合化*、**43**, 669-679(1985).

3) Synthesis of heterocyclic compounds using nitro ketene dithioacetal
Y. Tominaga and Y. Matsuda
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4) Synthesis of [2.2.3]cyclazines, aza[2.2.3]cyclazine and their related compounds
Y. Tominaga, Y. Shiroshita, and A. Hosomi
*Heterocycles*, **27**, 2251-2288 (1988).

5) ケテンジチオアセタールを利用する2-ピロンおよび2-ピリドン誘導体の合成
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*有合化*、**47**(7), 413-424(1985).

6) Synthesis of pyrimidine derivatives and their related compounds using ketene dithioacetals
Y. Tominaga, S. Kohra, H. Honkawa, and A. Hosomi,
*Heterocycles*, **29**(7), 1409-1429(1989).

7) アルコキシ置換高配位有機ケイ素化合物と高選択的ヘテロ環合成への応用
細見　彰、高良真也、富永義則、
*有合化*、**47**(9), 831-842 (1989).

8) Synthesis of heterocyclic compounds using carbon disulfide and their products
Y. Tominaga,
*J. Heterocyclic Chem.*, **26**(5), 1167-1204 (1989).

9) 不安定化学種等価体として機能する有機ケイ素化合物と高選択的ヘテロ環合成への応用
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台湾滞在記ー台南訪問—

薬学部昭和４４年卒業同窓会誌によせて：富永義則

台湾に来て６ヶ月が過ぎた。後一月無事に過ごせればと思いつつ 10 月に 65 歳を迎える。その頃連先生から台南（台湾の南西部の都市）行かないかと誘いを受け、気安くというか単純に反応して付いて行く事にした。一度は尋ねてみたいと思っていた台南である。実験をしようと気合いを入れての台湾での研究生活、観光気分とは少し違いも有った。これまでに台北市、淡水市を中心に日本統治時代の総督府をはじめ、オランダとの交流時代の色濃く残る紅城レストラン、台北市の小龍包で最も有名な鼎泰豐等々数々の名所史跡を案内してもらっている。何時ツツジが咲いたか、何時鮮やかな若葉が芽吹いたのか気に留める事無く実験に時を重ねての台湾暮らし、悔いなくこれまでやって来たと確かに言える。定年真近の気楽な暇つぶしと思われたかもしれないが、本人に至って真剣そのもの、それなりの緊張の連続、試薬が何処に有るか、器具が何処に有るか、廃液はどうすれば良いか、機器データーは自分で測定するのか、依頼するのか学生に聞かなければ成らない。相手の学生の雰囲気を計りながらの対応、これが以外と難しい。学生が、こちらの言動に気を使うのがわかる。全く場違いの他人の研究室での実験、どのような理由でこの実験室を使えるようになったのか、その経緯も分からないままのスタート、いちいち、これは使っていいでしょうかと尋ねてからの使用、試薬棚の試薬を使う場合はさらに気を遣う。後は結果を出すのみ、気楽ではない。その雰囲気は２ヶ月過ぎた頃から淡江大学化学科の先生達にも自然に理解してもらった。迷惑に思われないよう気遣ってきた。実験も直ぐに取りかかれるようろ紙をはじめ、ホットプレートスターラ、三角フラスコ、ナス型フラスコ等々簡単な最低限の器具を用意して来た。実験器具と言える程のものでないが本当に用意して来て良かったと思った。実験自体は、ただ試薬を混ぜるだけの実験で誰にでもできる世界一簡単な実験である。

実験は何から始めるか、それが問題だった。まずは、私達の研究結果に興味を持ったある化学会社の希望したテーマから始めた。それは溶液状態で緑色に光る発光化合物の合成だった。連絡を取り合っているうちに、緑の発光体を７月いっぱいで合成して欲しいとのこと。４月１日から実験ができるようにと淡江大学に連絡をしていたつもりが、４月１日に化学科を尋ねてみると、今日か

らゴールデンウィークで１週間休みと告げられる。学校に学生はまばら、研究室には入れない。どうなっているだと思いつつもこの事実を受け入れざるを得ない。１週間後すでに頼んでいた試薬は来ているかと尋ねれば、これから注文するとのこと。試薬は何時来るかと質問すれば、２ー３週間必要との事。さらに唖然。

試薬が手元に届いて原料合成ができたのが５月半ば、予定より一月遅れと成ってしまった。しかし会社からの依頼品は５月末には完成し、6月 14 日の淡江大学との共同の国際シンポジウムでの発表に間に合った。後は面白いばかり、楽しいばかり、色々な展開ができた。この結果は 7 月 24 日に開催された"3rd Keio University/Tamkang University Bilateral Symposium of Advanced Chemistry"での講演になった。

さらに９月半ばから次のテーマに取りかかった。何か面白くなりそう。しかし時間がない。今から試薬を頼めば１０月半ばに成ってしまう。それでも実験するか？　今回の本題に入ろう。

**台南を尋ねて**

台湾の西南部にある台南は、台湾の地名の由来にも成っている Tayowan と呼ばれる先住民族が住んでいた所。台南は台湾文化発祥の地と言われ、台湾を知るにはまず台南からと言われているみたいです。それで前述したように台北、淡水の北部はこれまでにも何回か案内してもらって知ってはいるが、多くの人が台北を中心とする北部はよく知っていると思いますので、今回尋ねた台南を紹介します。

まず、私が研究している場所は、台湾の北部、台北の北東部に位置する淡水川の河港にある人口５万くらいの中堅都市です。台北駅から地下鉄で３０分くらい。台南はこの台北から日本の協力で完成した新幹線で１時間 46 分くらいの所に有ります。まずその車窓から見える風景を紹介しながら台南まで行ってみます。

この新幹線は１５両くらいの連結だと思われたが確かではない。その５両目に乗った。台北は淡水川の北部以外は山に囲まれている。台北市は世界有数の高層ビル 101 に代表される高層ビル群が立ち並ぶ近代都市であるが、周りの山を抜けると緑深い山の中になる。しばらくする西側は広大で真平な平野が台南まで続く。こんなに広いとは想像していなかった。佐賀、筑紫平野よりも遥か

に大きい。台北から１時間程の所の台中まではそれなりの町で遠くには高いビルが有る。しかしビルの合間には田園が残っている。嘉義近くから次第に田園だけが見えてくる。見渡す限りの田園風景。大部分が稲作に見える。区画整理の進んだ近代的な田園で豊かさを感じる。日本でイメージしていた小さい区画の近代化から取り残された田園ではない。むしろ効率の悪い日本の方が遥かに遅れている。南部に行く程新幹線の駅近くは将来を期待して道路と広い土地が確保されている。駅の遠くにビルが見え、町はそこに有るのだろう。何か違和感が有る。全くの車社会想定の都市計画になっており不安はないのだろうか。

台南駅に着いても周りには新しく整備された道路はあるが商業活動の姿は見えてこない。周りにも全く見えない。ホテルのある街まで行くのに１時間ぐらい掛かった。22 階建ての西洋式最新のホテルであった。15 階のホテルの窓から高いビルが結構な数見える。大きな都市だろうと思われる。15 時頃に台北を出てこのホテルに着いたのが 17 時頃。18 時に夕食、ゴウジャスな夕食となった。

翌日、連先生の教え子の李夫妻に市内を案内してもらった。朝９時にホテルのロビーで待ち合わせ市内観光の始まり。この台湾大億ランデイスホテルの近くに多くの史跡が残っている。市定古跡台湾府城の大南門、鄭成功石像のある延平郡王祠、国定史跡のツカンロー、孔子廟、この廟の前にある門前町風の府中街、他にも日本時代の建物も残されている。午前中に回れたのはこれくらい。それぞれじっくり見てまわればそれなりに台湾の置かれた歴史がある。

その後も日本式庭園に日本式の立派な家屋が保存されている所、オランダ時代の城跡、清朝時代の史跡等々、これらが歴史の流れを感じさせない。そこに時代の区別なく、また統治者が誰であったかも意識する事なく、違和感もなく感じられるのは何故だろうと思う位、それぞれがしっかりと土着の文化に成っている。台北と違う、宜蘭や花連とも違う、この違いが大事と思う。

ここで一旦、李さんの実家でお茶をごちそうになる。中国式のお茶でゆっくり、ゆったり団らんの中にとけ込んで行く。この雰囲気が好い。それぞれの家を尋ねると必ず中国式のお茶を経験する。それぞれに自慢するセットを備え、それぞれの主人の歴史が刻まれている。ここでの話の中で突然に聞こえて来たのが剣道の竹刀の話、これらの竹刀は現在その７０ー８０％が台湾で作られている、との事、実際その竹刀をみせって貰った。帰り際にはその竹刀２本をニコニコしながら手に持つ事になる。よほど欲しそうな顔をしていたのだろう。しかし嬉しい。

虎頭埤

この日の夕食は台南の街中から１時間程車で行った山の中だった。ここの裏手の山から見る朝日が素晴らしいとのことだった。ここは山の中、山小屋風で我々６人以外は誰もいない。バーベキュ用の設備があちこちにある。またイノシシ料理用の石板が無造作に置いてある。我々６人は屋根のあるテーブルに陣取った。周りには２０個位のテーブルが有る。人気の店なのだろう。しばらくして暖められた黒っぽい壷が持ち込まれた。その中にメインの料理が入っているらしい。どうぞという事で真っ先に口にする事になる。分厚い角煮風の肉塊、口に入れてみる、肉独特の甘みはない、ゼラチン様の舌触り、ちょと苦みがある。悪くはない。これなら食べられる。スープも勧められる。普通の肉のスープではない。それといって魚でもない。

この料理の事を少し説明しておこう。先ほどの壷にヤギの肉とそれに色々な薬草を入れ石の竈で３日間じっくり煮込んだ薬膳料理だそうです。それでスープが若干苦みを持っている事に納得した。この他に通常の野菜料理とタケノコご飯が出て来た。タケノコご飯は炊き込みご飯の様な味がした。

今日の宿泊地はここからさらに山の中に入った所にある国民宿舎と同じような施設だった。今日は疲れた。布団に入り目覚めた時はもう朝だった。朝６時に連先生と散歩する事にした。ここの湖を一周するのに約１時間掛かるらしい。朝の散歩としては手頃。台湾に来て健康のためと良く大学の構内を散歩した。

センターから下の道路をみるともう沢山の人が急ぎ足で歩いている。一人だったり、二人だったり、また数人のグープもある。日本だったら初秋の湖畔の散歩だろうが、ここでは緑で青々している。台湾に秋はない。人も多い。入り組んだ入り江のような所には流木の塊がある。台風の影響らしい。路は適度に舗装されている。所々は木組み、木の道路に成っている。ちょと小高くなっている所は広く見渡せるように展望所に成っている。そこからみるとこの湖はかなり広い。朝食の後この湖を遊覧船で回る事になる。しばらく歩くと吊り橋が見えて来た。渡ってみる事にした。しかし橋の対岸に着くものと思っていたが途中で終わっていた。この橋も日本人が作ったとの事。新しくなっているがその土台は昔のままらしい。そこには丸い典型的な中国風の休憩所に成っている。若い男女の出会いの場所に成っているらしい。八方から気が集まる幸運の場所で、ここで願い事をすれば夢が叶うらしい。幸運は既に貰っている。昨日までの雨は止み、最高の旅行になっているのだから。水門の近くに来た。ここは土

手に成っている。今はセメント作り、かって洪水で決壊し相当数の犠牲者が出たらしい。日本人が作ったなら土手には柳が植えてある筈だが、ここには見当たらない。しかししばらく歩くと多くはないが確かに柳が有る。今の日本に柳の土手は見られない風景に成っているが、柳は八方に密度高く根を張り土手を頑強にする。この人工の湖がこの地の治水に役立ったか計り知れない。台北から台南までの大平野の治水の完璧さ、さらにこの湖の治水管理に驚きである。先人は賢い、すごい。一汗かいた１時間だった。

朝食のあと太陽電池で動く船でのクルジングを楽しみ、またコーロギの格闘技も見た。面白かったが、ちょっと残酷な気もした。

**草山３０８高地**

奇怪な山が有るという草山３０８高地に向かった。前日の疲れか、車の中ではついつい眠ってしまった。３０８高地の標識が見えた。もう大分の高さに来ている。曲がりくねった、車一台がやっと通れるような山道を登った所は、もう全くこれまでの台南での経験では考えられない風景になっている。眼下は三角型の緑色まじりの灰色のとんがりの帽子を並べたような山並みになっている。のこぎりの刃を上にしたような光景でもある。それが遠くまで、遠くにかすむビルの建物の所まで続いている。目線が下に有るためか空が非常に広く感じられる。右手の方は高雄市の方角と思う、台地の形をした山の麓まで、左は台南市方角、今日は天気に恵まれている。遠くまでその光景は続いている。最も眼下に近い所の山は左側、つまり北側は緑のリボンで縁取りをしている。南側はそれぞれの山の急斜面で灰色、砂の色、その谷底には一部緑が有り川が流れている。また人家も有るみたい。この風景が見渡す限りの視界にある。村上春樹の小説「IQ８４」の月の風景や加藤まさをの「月の沙漠」の情景が浮かんでくる。この風景に月がぴったり来る。

このような句はどうだろう。

砂山の大海にうかぶ月あかり

この景色の中でビールを飲みながら、台湾料理を楽しみ、ただ見ているだけ。食べては遠くを眺め、また食べる。しかし何を食べたかは覚えていない。しばらくすると世界遺産にはどうだろうという話になった。皆納得。なんとかしたい雰囲気に成る。この壮大なパノラマを後に台北への帰途につく準備をしていると急に霞が掛かり何も見えない。舞台の幕が下ろされた。なんと不思議！

本当に楽しい思い出に残る台南への旅行でした。これ以上の表現は私には無理です。是非一度尋ねてみてください。　　（平成２２年１０月１２日）

# 謝　辭

（於淡江大學之寶貴經驗）

托大家的福，讓我能在淡江大學平安的渡過七個月有意義的學園生活，對於各位的溫馨支援與協助，於此謹致由衷謝意。

若將學生時代算在內，我在長崎大學的研究生涯至明年三月將滿 45 年。在退休前一年的七個月歲月裡，能夠專心的從事我終生事業的 ketene dithioacetal 研究，真是幸福之至。

我的研究是無論國中生或高中生，只要有興趣誰都能輕易完成的實驗，而此簡易實驗卻能完成最新研究，則是讓我引以為傲之事。當初就是因此才選擇化學系來作為實踐此一目標之場所。至此為止所執行研究，都是以簡單、廉價、小規模為基本，進而追求社會性高之相關實驗。

第一次到台灣之際，正在進行的捷運地下化工程，讓我感受到台北車站即將會有重大的轉變。那年（1995 年）是來參加於台北舉行的第 15 屆國際雜環化學研討會（兩年舉辦一次的該研討會，於 2011 年將在英國舉行第 23 屆）。那年是我完成在美國南佛羅里達大學卡斯魯教授研究室的第二次留學，並且剛返日本開始研究的時候。該次所發表的內容為 luminol type 化學性發光物質之合成化學研究。經過之後將近 15 年的時間，將研究往螢光性發光物質的方向深化，進而能在淡江大學進行最後的修潤補強工作，於此謹對讓我能夠順利完成實驗的淡江大學化學系再次表示感激之意。

最近登上世界性新聞報導的兩位日本人，北海道大學的鈴木章名譽教授以及旅居美國的根岸英一博士獲頒諾貝爾獎。我所任職的長崎大學之前輩下村修博士於 2008 年獲頒諾貝爾獎等相關新聞，在在的顯示著最近日本人的活躍相當顯著。這些前輩們經都歷過昭和 30 年代、1960 年代前後，充滿著夢想與希望的日本高度成長年代。

日本至此終於從北（北海道）到南（九州），都有諾貝爾獎得者的誕生。此事對於日本而言極具重要意函，亦即有意義的研究並非僅止於東京或大阪等大都會，而是將化學領域分散的擴及地方型大學，想必是因有此基礎的支援才有如此的顯著結果。台灣的大學亦多屬地方型，一旦能夠活化成個性豐富的大學，想必亦能成為世界性的著名大學。衷心的期盼與祝福。（以上譯自富永教授日語原文）

感謝淡江大學給予我有意義的七個月的研究生活。更感謝化學系各位教授給我研究的機會，加深研究內容以及增進『心的交流』，對大家表示衷心的感謝。

2010 年 10 月 25 日

於 台灣、淡江大學 理學院 化學系

長崎大學教授、淡江大學客座教授　富永義則

感謝のことば
（淡江大学での貴重な経験）

淡江大学で無事７ヶ月間の学園生活を無事に過ごす事ができました。これも皆様方の温かいご支援とご協力のお蔭と心より感謝申し上げます。

私は来年の三月を持ちまして、学生時代を合わせ45年間の長崎大学での研究生活を終えます。その最後の年に７ヶ月もの長い間、私のライフワークとしておりますケテンジチオアセタールの研究に没頭できた事を本当に幸せに思います。私の研究は、中学生や高校生でも、興味さえ有れば誰でも簡単にできる実験です。また最新の研究ができるものと自負しております。その実践の場にこの化学科を選択させてもらいました。これまで研究遂行の基本として簡単、安価、小スケール、それに社会性の高い実験を追求して参りました。

最初に台湾に来たのは、まだ地下鉄が工事中で台北駅近くが大きく変わろうとしていた時ではなかったかと思います。それは1995年の第15回国際複素環化学討論会（来年はイギリスで２年ごとの23回大会）が開催され、南フロリダ大学のキャスル教授の所での２回目の留学を終え、日本で研究を再開したときです。この時の発表が、ルミノールタイプの化学発光性物質の合成化学的研究です。それから15年近くたって、研究を蛍光性発光物質の研究へと深化させ、さらに最後の仕上げとして、ここで実験ができた事に感激しております。

最近、世界的なニュースとして二人の日本人、鈴木章北海道大学名誉教授とアメリカ在住の根岸英一博士がノーベル賞を受賞されました。2008年には長崎大学の先輩下村修博士が受賞されるなど最近日本人の活躍が目立っています。これらの人は日本の高度成長時代、昭和30年代、1960年代前後からの夢と希望があった時代を経験しております。

これでノーベル賞が日本の北から南まで全体から生まれた事になります。この事が日本にとって非常に重要な意味をもちます。意義ある研究が東京に、大阪に集中されるのでなく地方に分散し化学の裾野を広げ、その土台を支えた結果があるからだと真に思います。台湾でも地方が、個性豊かな大学が活性化したとき世界的になると思います。期待しております。

感謝淡江大学給予我有意義的七個月的研究生活。
更感謝化学系各位教授給我研究的機会，加深研究内容，増進「心的交流」
對大家表示衷心的感謝。
謝謝。

２０１０年１０月２５日
台湾、淡江大学理学部化学科において
長崎大学教授、淡江大学客員教授　富永義則